October 1955 Pages 569-640

The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 71 Number 10

CONTENTS

PROCEEDINGS OF THE SOCIETY
The Principles and Practice of the Flameproofing of Textiles (*F. Ward*) 569
Cellulose Acetate and Water Repellency (*R. J. Mann*) 579
PUBLICATIONS SPONSORED BY THE SOCIETY'S FASTNESS TESTS CO-ORDINATING COMMITTEE
XVI—An Investigation into some Methods for the Assessment of the Weathering Fastness of Dyed Textiles (*E. Butterworth and J. C. Guthrie*) 587
COMMUNICATIONS
The Chemistry of Esters of Leuco Vat Dyes—I (*S. Ainsworth and A. Johnson*) 592
The Dyeing of Acetate Rayon with Disperse Dyes IV—Adsorption Isotherms (*C. L. Bird and F. Manchester*) 604
CORRESPONDENCE 609
NOTES 610
NEW BOOKS AND PUBLICATIONS 612
MANUFACTURERS' PUBLICATIONS AND PATTERN CARDS 617
ABSTRACTS 619

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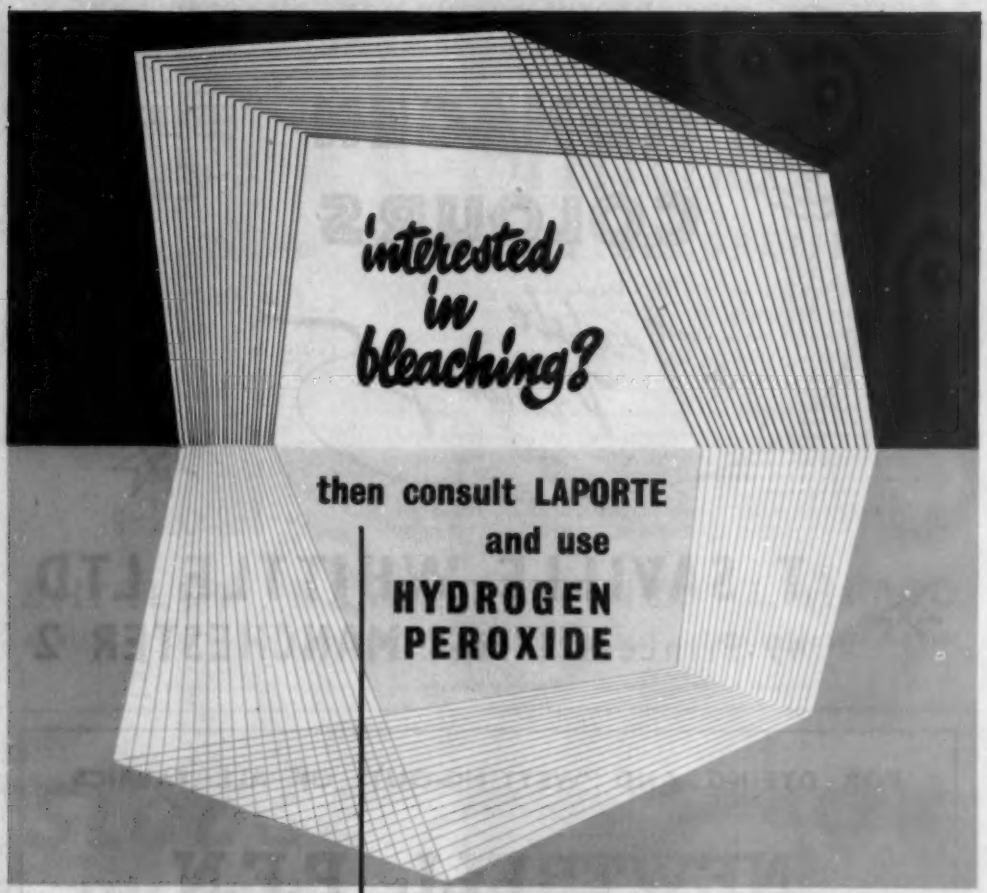

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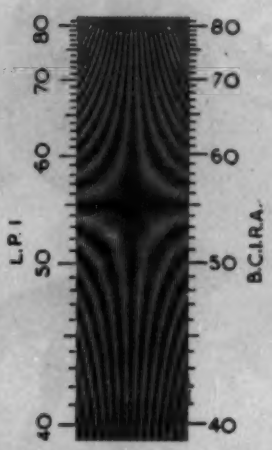

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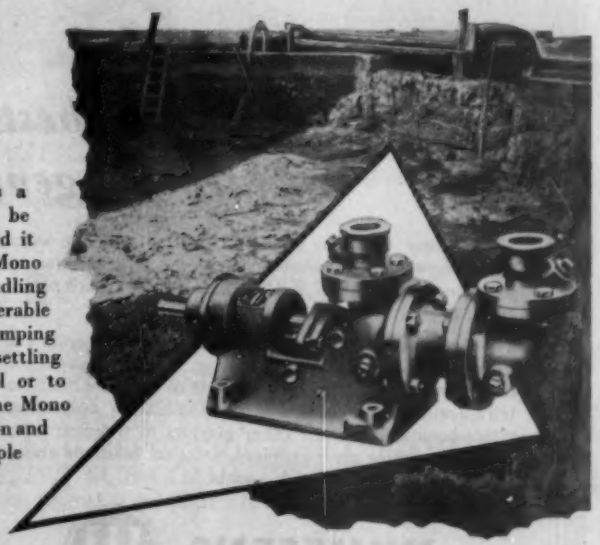

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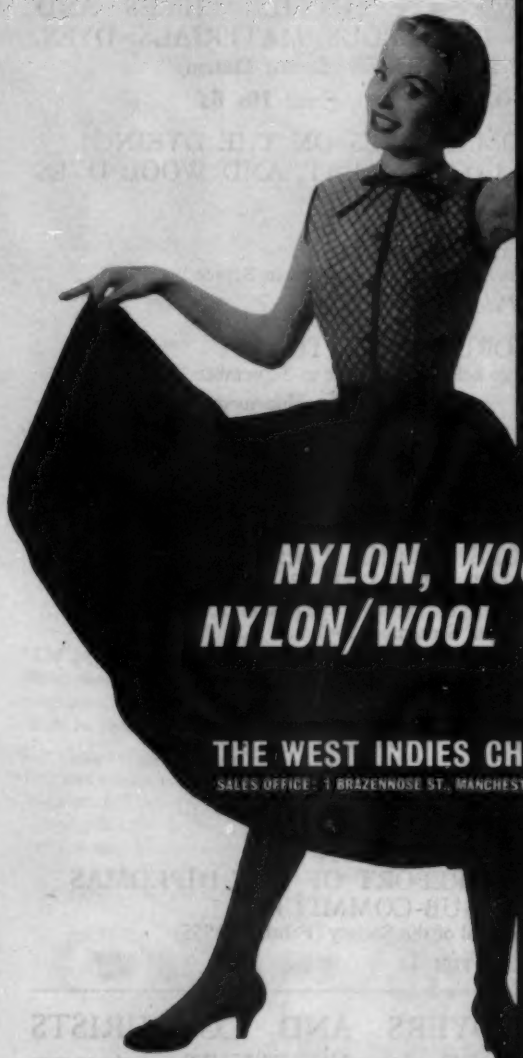

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1955 and pages 369–372 of the July 1955 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal* —

LECTURES

Printing of Wool including the Production of Mélange Effects	*J. A. Potter*
Some Observations on American Bleaching and Dyeing Processes	*J. K. Skelly*
Estimation of Fluorescent Brightening Agents	*G. G. Taylor*
The Use of Silicones in the Textile Industry	*T. W. Watson*

COMMUNICATIONS

The Rotproofing of Viscose Rayon
I — Treatment of Viscose Rayon with Formaldehyde and Formaldehyde-containing Resins — *J. W. Bell, M. M. Ramsey, and C. S. Whewell*

The Polarography of Azo Dyes — *J. de O. Cabral and H. A. Turner*

The Adsorption of Some Organic Vapours by Wool and Nylon — *H. R. Chipalkatti, V. B. Chipalkatti, and C. H. Giles*

The Irgalan Dyes — Neutral-dyeing Metal-complex Dyes — *G. Schetty*

EXPLANATORY PAPER ON MODERN THEORY

An Introduction to the Theory of Wool Dyeing
II—The Kinetic Approach — *L. Peters*

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FORTHCOMING MEETINGS OF THE SOCIETY

Monday, 24th October 1955

BRADFORD JUNIOR BRANCH. *Fading — Its Nature and Assessment.* H. B. Mann, Esq., M.Sc. (Courtaulds Ltd.). Technical College, **Bradford.** 7.15 p.m.

Tuesday, 25th October 1955

SCOTTISH SECTION. *Kier Boiling.* C. Garrett, Esq., F.T.A. St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 26th October 1955

MIDLANDS SECTION. *Textile Bleaching with Peroxide and Peracetic Acid.* L. Chesner, Esq., B.Sc., A.T.I., and G. C. Woodford, Esq. College of Technology, **Leicester.** 7 p.m.

Thursday, 27th October 1955

NORTHERN IRELAND SECTION. *Fire Prevention Methods in the Textile Industry.* Film will be shown. J. R. Coulter, Esq. Thompson's Restaurant, Donegall Place, **Belfast.** Joint meeting with Textile Institute. 7.30 p.m.

WEST RIDING SECTION. *The Dyeing and Finishing of 'Courpleta'.* W. R. Beath, Esq., M.Sc., and J. S. Ward, Esq., B.Sc. (Courtaulds Limited). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 4th November 1955

LONDON SECTION. *Microscopical Investigations of Fibre Damage.* G. G. Taylor, Esq., and J. C. Brown, Esq. (Clayton Dyestuffs Co. Ltd.). Joint Meeting with the London Centre of the Guild of Dyers and Cleaners. The Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6.30 p.m.

Tuesday, 8th November 1955

BRADFORD JUNIOR BRANCH. *Microscopical Investigations of Fibre Damage.* G. G. Taylor, Esq., and J. C. Brown, Esq. (Clayton Dyestuffs Co. Ltd.). Technical College, **Bradford.** 7.15 p.m.

LONDON SECTION. *The Design and Production of Furnishing Fabrics.* H. Woodman, Esq., A.T.I. (Warner & Sons Ltd.). The Chemical Society, Burlington House, **London, W.1.** 7 p.m.

Wednesday, 9th November 1955

NORTHERN IRELAND SECTION. *The Dyeing of Terylene Polyester Fibres.* H. R. Hadfield, Esq., M.Sc. (Tech.) (Imperial Chemical Industries Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 10th November 1955

WEST RIDING SECTION. *Light Fastness Testing and the causes of Anomalous Fading.* K. McLaren, Esq., B.Sc., F.R.I.C., F.S.D.C. (Imperial Chemical Industries Ltd.). The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Saturday, 12th November 1955

MIDLANDS SECTION. Ladies' Evening — Dinner Dance. Welbeck Hotel, **Nottingham.**

Tuesday, 15th November 1955

HUDDERSFIELD SECTION. *The Problems of the Garment Dyer and Finisher.* B. Kramrisch, Esq. and F. Grainger, Esq. Co-operative Cafe, **Huddersfield.** 7.30 p.m.

Friday, 18th November 1955

HUDDERSFIELD SECTION. Annual Dinner. Co-operative Cafe, **Huddersfield.**

MANCHESTER SECTION. Ladies' Evening — Full details later.

Tuesday, 22nd November 1955

SCOTTISH SECTION. *The Dyeing and Finishing of 'Courpleta'.* W. R. Beath, Esq., and J. S. Ward, Esq. (Courtaulds Ltd.). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 23rd November 1955

MIDLANDS SECTION. *Modern Methods of Finishing Open-width Knitted Fabrics.* Film Evening introduced by J. Dalglish, Esq. Technical College, **Nottingham.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Properties of Terylene/Wool Blends in Yarn and Fabric Form.* B. I. Brooke, Esq. (I.C.I. 'Terylene' Council). Technical College, **Bradford.** 7.15 p.m.

Thursday, 24th November 1955

WEST RIDING SECTION. *The Newer Developments in the Field of Sulphur Dyestuffs.* H. Musshoff, Esq. (Cassella Farbwerke Mainkur A.G.). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 2nd December 1955

LONDON SECTION. *The Application and Evaluation of Optical Bleaching Agents.* G. R. Perdue, Esq. (British Launderers Research Association). The Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

Wednesday, 7th December 1955

MIDLANDS SECTION. *The Dyeing and Finishing of 'Courpleta' Knitted Fabrics.* S. N. Bradshaw, Esq. Bell Hotel, **Leicester.** 7 p.m.

Thursday, 8th December 1955

WEST RIDING SECTION. *An Outline of the History of the Finishing of Wool Cloths.* C. O. Clark, Esq., F.T.I., F.S.D.C., Chairman, Preservation of Historical Records Committee. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 9th December 1955

MANCHESTER SECTION. *The Causes of Felting in Rayon Textiles.* H. W. Best-Gordon, Esq., F.C.I. The Textile Institute, 10 Blackfriars Street, **Manchester 10.** 6.30 p.m.

Tuesday, 13th December 1955

SCOTTISH SECTION. *Basic Mechanism in Jigger Dyeing of Woven Fabrics.* Dr. J. Ashworth (Courtaulds Ltd.). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 14th December 1955

NORTHERN IRELAND SECTION. *Recent Developments in Bleaching, Dyeing and Finishing Machinery.* K. Laurie, Esq. (John Dalglish & Co. Ltd.). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 15th December 1955

BRADFORD JUNIOR BRANCH. *Experience in the Application of Automatic Regulation to the Dyeing Process.* F. Blezzard, Esq. (Drayton Regulator & Instrument Co. Ltd.). Technical College, **Bradford.** 7.15 p.m.

Tuesday, 20th December 1955

HUDDERSFIELD SECTION. *The Dyeing of 'Courpleta'.* W. R. Beath, Esq. and J. S. Ward Esq. (Courtaulds Ltd.). Co-operative Cafe, **Huddersfield.** 7.30 p.m.

Wednesday, 11th January 1956

NORTHERN IRELAND SECTION. *Causes of Felting in Rayon Textiles.* H. W. Best-Gordon, Esq. (Courtaulds Ltd.). (Joint Meeting with the Textile Institute), Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 12th January 1956

WEST RIDING SECTION. *User Dyer Relations.* I. Glasman, Esq., A.T.I. (Marks & Spencer Limited). The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 13th January 1956

LONDON SECTION. Details later.

BRADFORD JUNIOR BRANCH. Lecture Title to be announced later. Midland Silicones Ltd. Technical College, **Bradford.** 7.15 p.m.

Tuesday, 17th January 1956

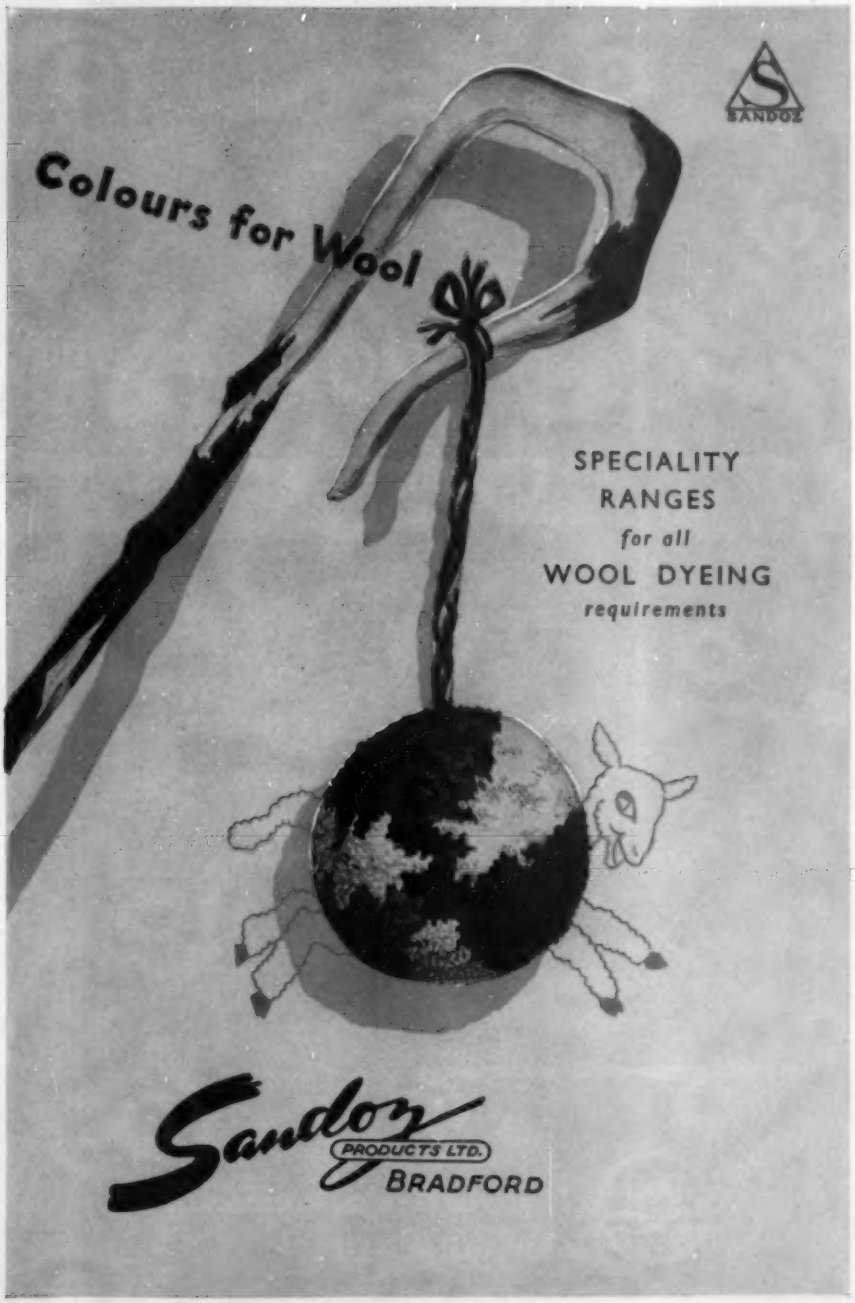
HUDDERSFIELD SECTION. Title later. Professor J. B. Speakman.

SCOTTISH SECTION. *What Dyeing does to Wool.* F. F. Elsworth, Esq., Ph.D., A.R.I.C., F.S.D.C. (Wool Industries Research Association). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 18th January 1956

MIDLANDS SECTION. Discussion Group on *Detergency.* Questions invited. G. H. Rostron, Esq., A.R.I.C. (Soap), R. C. Tarring, Esq., B.Sc., A.R.C.S. (Synthetics), and R. S. Hartley, Esq., A.R.I.C. (Research). Kings Head Hotel, **Loughborough.** 7 p.m.

continued on page xxxi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THE JOURNAL
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Volume 71 Number 10 OCTOBER 1955 *Issued Monthly*

Proceedings of the Society

The Principles and Practice of the Flameproofing of Textiles

F. WARD

Meetings of the London Section held in the rooms of the Royal Society, Burlington House, London W.1, on 6th February 1953, Mr. G. F. Wood in the chair; and of the Manchester Section held at the Textile Institute, Manchester, on 16th October 1953, Mr. J. Boulton in the chair

The flameproofing of textile fibres and fabrics is considered in all its aspects.

Flammability and associated properties are defined. The methods at present available for rendering cellulosic fibres flameproof are described—soluble finishes, the so-called "permanent" ester finishes, precipitation treatments, and coatings. The flameproofing of cellulose acetate, wool, nylon, and blends is also discussed.

A new theory is suggested for the basic mechanism of the burning and flameproofing of fabrics. The methods of testing flammability and related properties are critically described, and the difficulty of interpreting laboratory data in terms of actual fire hazard is shown.

Some new data on the ignition temperatures and vertical burning rates of a series of fibres are given.

1. INTRODUCTION

Definitions

A *flameproof* fabric may be defined as one which does not propagate flame, although it may burn or char when subjected to any form of heat. This definition is not absolute, since it depends on the method of testing. The term is, however, more acceptable than *fireproof*, which tends to imply that a material cannot be destroyed by heat. Clearly, no proofing treatment can prevent organic textiles from being destroyed by heat.

A fabric may be flameproof and yet glow after removal of the source of heat. This effect is classified as *afterglow* or *flameless combustion*. It may cease after the char has been consumed, or the afterglow may consume the whole fabric (flameless combustion). A fabric is termed *glowproof* when there is no afterglow or when it ceases to glow within a stated number of seconds.

On these definitions, the only untreated fibres which may be termed flameproof are—alginates, glass, asbestos, Saran, and dynel, none of which has a wide field of use. Wool, casein, and other protein fibres, although inflammable, are not considered serious fire hazards, owing to their relatively high ignition point and comparatively slow flame propagation rate. The thermoplastic fibres are difficult to classify, as they melt and shrink away from the flame; but it is clear that nylon and Terylene are much less flammable than viscose rayon, acetate rayon, cotton, linen, and Orlon, all of which burn readily. The practice of flameproofing textiles, therefore, generally concerns aftertreatment of this last group of fibres.

Historical Development

The desirability of reducing the flammability of readily combustible material has been recognised for over 2000 years[1, 2]. It is related that Aeneas in the fourth century B.C. recommended the use of vinegar to impregnate wood; and, according to the annals of Claudius, the wooden storming-towers at the siege of Piraeus in 83 B.C. were protected by treatment with a solution of alum.

Records of the treatment of fabric are of comparatively recent date. One of the earliest is a book by Sabattini, published in 1638, dealing with the fire risk in theatres; in this the use of clay and plaster of Paris in the paint applied to the canvas used for decorative purposes is recommended. In the records of "Early Science at Oxford", 16th September 1684[3], it is reported that "Merchant Wayt's account of his piece of Incombustible cloth was read".

The first relevant English patent was granted in 1735 to Jonathan Wyld[4] for a flameproofing mixture containing alum, ferrous sulphate, and borax. About this time, Montgolfier is reputed to have treated his balloons with alum. Then in 1786 Arfird suggested the use of ammonium phosphate —still a constituent of many flameproofing mixtures.

The first serious investigation of the possibilities of flameproofing textiles appears to have been carried out in 1820 by Gay Lussac at the instigation of Louis XVIII of France. Lussac treated hemp and linen fabric: from his researches he concluded that the most effective salts were those which gave off non-inflammable vapours on heating or covered the fabric with a glassy layer.

Some years later Versmann and Oppenheim studied the effects of a large number of chemicals and concluded that only five salts and mixtures had practical value—ammonium phosphate, ammonium sodium phosphate, ammonium sulphate, sodium tungstate, and a mixture of ammonium phosphate and ammonium chloride. They also patented, in 1859, a process of flameproofing by the precipitation of stannic oxide in the fibre [5].

Perkin did extensive work on the production of permanently flameproofed cellulose and, in the early 1900s, developed the "Non-flam" process. This was undoubtedly a modification of the Versmann and Oppenheim patent. He claimed [6] that the production of permanently flameproofed cotton flannelette had been successfully solved.

By this time most of the suitable salts had been recognised as flameproofing materials. In 1922, Kling and Florentin [7], working in France, found that a solution of borax and boric acid in the ratio 6 : 5 gave very satisfactory results. A few years later Ramsbottom and Snoad, in an extensive study of flameproofing mixtures, confirmed this finding but preferred a ratio of 7 : 3, which gave a non-crystallising mixture. This latter treatment has received official recognition, despite the quite appreciable afterglow which results from its use [8].

Research in recent years has been devoted largely to the development of a treatment for cellulose which will resist washing. Some success has been achieved, but no completely satisfactory process has yet been used commercially.

Legislation and Regulations

In England the only regulations dealing with the flameproofing of fabrics apply to public places and are controlled by the County Councils. Despite the number of accidents and the loss of life caused by the use of inflammable material for clothing, no official action has been taken to control the sale of dangerously flammable apparel textiles.

The problem has, however, been considered. In 1908, following the introduction of flannelette, which was considered to contribute to the great increase in the number of burning accidents involving children, a Home Office enquiry was instituted to consider clothing fire hazards and to report on the merits of certain non-inflammable materials, e.g. the Non-flam process, which had been introduced by Perkin but which had not won popular favour. The commission merely recommended that the public should be protected from the sale of fabrics which were misrepresented as being flameproof, and the Fabrics Misdescription Act followed in 1913 [9].

From that time until the 1939–1945 war there was little interest in flameproofing clothing, except for special purposes. The war, however, produced a demand for the flameproofing of textiles for the armed forces such as uniforms, and in the Navy for treatment of hammocks, anti-flash gear, boat covers, etc. This demand stimulated research into the possibility of producing a permanent flameproof finish.

As far as ordinary clothing is concerned, only certain types of materials such as raised fabrics and light-weight nets constitute a really serious hazard, but the type of garment into which the material is made is a contributory cause, women's clothes being a greater danger than men's [9, 10]. Deaths due to a dress catching fire by contact with an electric heater are all too frequently reported. Dr. and Mrs. D. Colebrook have stated [9] that, each year, not less than 100 children in England and Wales owe their death primarily to the fact that their clothes *easily* catch alight on touching a fire; and that many times this number are seriously burned, a large proportion being permanently disfigured.

Appreciation of this risk of personal danger appears to be greater in the U.S.A., where attempts have been made to prevent the sale of fabrics which are dangerously inflammable. A law was passed by the Californian legislature in 1945 to control the sale of dangerous fabrics, but the difficulties encountered in agreeing to a standard were so great that it had to be amended several times. Bills were also introduced into Congress but were not proceeded with. However, after extensive work, agreed commercial standards were published in 1952: these form the basis of a Federal law [11], which came into effect in June 1954, prohibiting trade in highly inflammable fabrics.

Flammability of Fabrics

The flammability of a fabric is largely controlled by its construction and the yarn from which it is made. The finer the thread and the more open the weave, the more readily will the fabric ignite; and conversely, the coarser the yarn and the tighter the weave, the less flammable the fabric.

The most readily inflammable materials are thus fine nets and raised fabrics, especially if the pile is long. The inflammability of some of these materials could be appreciably reduced if they were made from yarns of coarser denier. For example, experiments have shown that there is a great increase in flammability when 1¼-denier Fibro is used in place of 4½-denier. The same is true of other fibres.

2. TREATMENTS FOR CELLULOSE

Requirements

A practically useful flameproofing material should not—

(1) tender the fabric, either during or after treatment

(2) crystallise on the surface of the fabric when subjected to varying humidities

(3) require an addition of more than 15–20% on the weight of the fabric

(4) spoil the handle of the fabric

(5) be poisonous or dermatologically harmful

(6) produce afterglow.

Surface crystallisation does not appear to have worried the early experimenters, since most of the numerous mixtures recommended by them crystallise on the surface. (The effect may not have been very noticeable, since they were working with cotton.) It is important, however, not only because it spoils the appearance of the fabric, but also because the crystals may be removed by mechanical treatment, with a resultant loss in flameproofing properties. The difficulty is overcome by using a mixture which dries down to a glass. Treated fabrics may be tested for crystallisation by hanging a cutting in a desiccator over saturated salt solution (which maintains a relative humidity of 75%) for 12–24 hr., and then allowing the fabric to dry slowly in the air. The test should be repeated several times on the same cutting.

Treatments may be conveniently divided into those which are reasonably fast to water and those which are completely removed by washing.

The simplest method of flameproofing is the application of soluble salts or their mixtures, but the above requirements rule out the use of a large proportion of the effective materials.

Water-soluble Treatments for Cellulose

Of the many scores of mixtures suggested, few have been used commercially, for a variety of reasons. For example, ammonium salts such as the chloride and sulphate are liable to cause tendering on storage. Salts like calcium chloride, magnesium chloride, and zinc chloride are undesirable for the same reason, and in addition are deliquescent. Alum, again, is not very efficient, and is undesirable because of its acid reaction. Many of the other mixtures which have been suggested are also unsatisfactory because of afterglow or surface crystallisation.

Most flameproofing solutions are mixtures of two or more salts, since, with the possible exception of ammonium sulphamate, no solution of a single salt will satisfy all the requirements given above. Ammonium sulphamate[12], introduced commercially about fifteen years ago, was for a time recommended for flameproofing; but it achieved a reputation for tendering the fabric, and went out of favour. Recent unpublished work, however, suggests that it is probably no worse than any other treatment which leaves the fabric slightly acid. The early results were probably due either to impure samples of ammonium sulphamate or to drying at too high a temperature.

A mixture should be as simple as possible; preferably, only two salts should be used, and never more than three. This is particularly important when a stock solution is to be maintained. Frequent additions of chemicals to the solution, unless carefully controlled, may result in slight variations in the proportions of the constituents; although this may not affect the flameproofing properties, it may render the treatment prone to surface crystallisation.

Treatment of fabrics made from cotton, viscose rayon, or mixtures of the two fibres presents no difficulty in processing, provided that they have been well scoured. The precise strength of the solution required can be ascertained only by experiment, for it will depend on the structure of the fabric and on whether the fabric is made from cotton, viscose rayon, or a mixture of the two. The heavier the fabric, the less loading will be required. The treatment may produce a slight change in colour, so that it is advisable to treat a small pattern before carrying out bulk treatment.

In all cases the dyed fabrics are either treated on a winch or padded (preferably the latter), and then dried on suitable machinery at as low a temperature as possible. Drying should be carried out with care, as too rapid heating may cause crystallisation of even the best mixtures, and if an ammonium salt is used some loss of ammonia may result.

It is easier to handle dry goods, but fabrics can be treated wet, although it may be necessary to pad twice in order to obtain the correct concentration of salts in the dry fabric.

One of the best-known mixtures contains borax and boric acid in the proportion of 7 parts borax to 3 parts boric acid, as was recommended by Ramsbottom and Snoad[8]; usually a loading of 10–15% is sufficient. This treatment produces a well flameproofed fabric, but there is some afterglow. No surface crystallisation occurs with this mixture, as a glass is formed on evaporation[13].

Another mixture, which has the added advantage of being glowproof, consists of ammonium dihydrogen phosphate and borax in the ratio of 2 : 3. When experiments (unpublished) were being carried out to determine the most suitable ratio of the two salts, it was found that, although flameproof results were obtained with a wide range of ratios, it was only within a very narrow range that the mixture was non-crystalline.

Zinc chloride is a very efficient flameproofing agent and there is no afterglow; but it cannot be used alone because it is deliquescent and has an acid reaction. This difficulty is overcome by a mixture patented in 1918[14], which appears to have been little used. It consists of zinc chloride and zinc phosphate dissolved in excess of ammonia, and depends for its success primarily on the formation of zinc ammines, $ZnCl_2,xNH_3$. The zinc phosphate is not essential, and a suitable solution can be made by dissolving 180 g. of zinc chloride in 500 c.c. of water, adding ammonium hydroxide until the precipitate formed is redissolved (about 400 c.c. of ammonia (sp.gr. 0·880) will be required), and diluting to 1 litre. This solution is sometimes referred to as "ammonium zincate", but is truly a solution of a zinc ammine. This is a very efficient method of flameproofing, but it has the disadvantage that, if care is not taken during drying, some dulling of the fabric may take place owing to the formation of zinc oxide. It is also essential that no copper be present in the finishing machinery, otherwise there is a risk of blue marks being formed

on the fabric. It has been used commercially on a very light Tenasco fabric, on which other treatments were ineffective.

Another mixture which was used successfully for many years is—15 parts sodium tungstate, 8 parts boric acid, 8 parts ammonium dihydrogen phosphate, and ca. 70 parts water. The solution is used at between 32°Tw. and 38°Tw. according to the fabric to be treated. Owing to the high cost of sodium tungstate, the process is no longer economic.

Permanent Treatments for Cellulose

Attempts have been made to produce permanently flameproofed fabrics by at least three methods. The most important of these are—

(a) Modification of the cellulose
(b) Precipitation of an oxide within the fibre
(c) Coating the fabric with a resin containing certain oxides.

Examples of these treatments are given below.

(a) Modification of the Cellulose

The simplest method of modifying cellulose is by esterification. Numerous esters of cellulose have been made, but the only commercial one used as a textile is cellulose acetate. Since cellulose acetate burns readily, attention was directed to the formation of the inorganic esters such as the sulphate and the phosphate.

Numerous references to both cellulose sulphate[15] and cellulose phosphate[16] are to be found in the literature, but the methods of producing them are not generally applicable to textile finishing. The cellulose sulphate formed by most methods is a water-soluble compound.

It was not until the 1939–1945 war that the partial esterification of cellulose fabrics with inorganic acids became practicable. Joseph Bancroft & Sons Co.[17] in the U.S.A. developed a treatment using urea and phosphoric acid, and later Courtaulds Ltd.[18] developed one using cyanamide and phosphoric acid, or cyanamide and sulphuric acid.

The Bancroft process was modified to use ammonium salts. An example quoted by Little[19] uses a solution of diammonium phosphate and urea; the fabric is padded, dried, and heated at 175°C. for about 7 min., washed off, and dried. By this means 10–15% esterification is achieved quite easily, but severe tendering of the fabric takes place. This process has been operated to a limited extent in America, and some trials have been carried out in Great Britain.

In the Courtaulds process, cyanamide can be used with the free acid, although it is better to add some ammonium sulphate, as the solution is more stable. With this type of mixture a much lower temperature of baking is required, with the result that less tendering occurs. It is also possible, by this treatment, to produce a partly esterified cellulose containing up to 20% sulphuric acid. The reaction is extremely efficient.

In both cases the salt of ammonium or the nitrogenous base with the acid cellulose ester is formed, and provided that at least 10% esterification takes place, a well flameproofed material is produced. There is a slight afterglow with the sulphate, but none with the phosphate.

Typical treatments are as follows—

1. Pad the cellulosic fabric through a solution containing—

Sulphuric acid (15 *N.*)	15 litres
Ammonium sulphate	5 kg.
Cyanamide soln. (28%)	50 litres
Water	30 litres

Dry, and bake at 105°C. for 5 min.; wash off in weak alkali and dry. The fabric is well flameproofed, but there is some afterglow.

2. Pad the cellulose fabric through a solution containing—

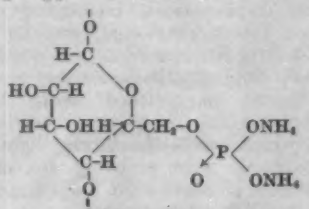
Phosphoric acid	10 kg.
Ammonium dihydrogen phosphate	14 kg.
Cyanamide solution (28%) ...	62 litres
Water	14 litres

Dry, and bake at 105°C. for 5 min.; wash off in weak alkali and dry. The fabric is well flameproofed, and there is no afterglow.

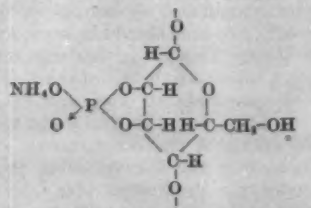
These treatments are stable to water, but the fabric gradually becomes flammable after repeated washings, owing to the formation of the sodium salts of the cellulose esters, since the acid esters of cellulose are base-exchange materials. (Similarly, treatment with calcium salts produces the calcium salt of the cellulose ester.) The fabric can be made flameproof again by treating in weak ammonium chloride for a short time.

If cellulose is esterified till it contains about 20% sulphuric acid, it is flameproof even when converted to the sodium salt, but at this point the fabric becomes highly swollen, with an imbibition greater than 150%. The fabric may become water-soluble if the esterification is carried still further. Cellulose phosphate obtained by this type of treatment has a reduced imbibition, as some cross-linking of adjacent cellulose chains takes place, and this, under certain conditions, can give rise to crease-resistant properties.

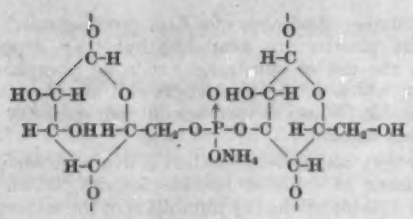
Schematic formulæ for the phosphate and sulphate esters of cellulose are given below (following Coppick and Hall[20])—



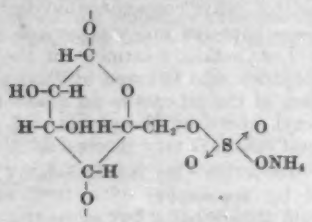
Monocellulose diammonium phosphate



"Dicellulose" monoammonium phosphate



Cross-linked dicellulose ammonium phosphate



Monocellulose ammonium sulphate

Mixed esters can be produced by the use of mixtures of phosphoric acid and sulphuric acid, but it is not possible by this means to reduce the imbibition to a useful low value. An imbibition of 150% has been found with a treated fibre, insoluble in cuprammonium solution, containing both sulphuric and phosphoric acid.

It is also possible to add formaldehyde to the treating solutions, with a resultant improvement in strength retention and a corresponding reduction in extension.

Two commercial treatments which produce similar results are (i) the Pyroset (American Cyanamid) and (ii) the Pyrovatex (Ciba) processes. Both give well flameproofed but rather brittle fabrics.

Other methods of modifying the cellulose fabric include that developed by the Southern Regional Laboratories of the U.S. Department of Agriculture; this uses tetrakishydroxymethylphosphonium chloride $P(CH_2OH)_4Cl$ (abbreviated T.H.P.C.). The process, which has now been developed sufficiently to be commercially feasible, has been extensively described in the literature[21]. A suitable treatment for a cotton twill is to pad through a solution containing 15·8% T.H.P.C., 9·5% methylolmelamine, 3% triethanolamine, and 9·9% urea, and then to dry, bake for 4·5 min. at 140°c., and wash off. The resultant fabric is well flameproofed and free from afterglow. There is some loss in strength, but not sufficient to prevent the process from being applied to most types of fabric. The finish also produces some crease- and shrink-resistant properties, and is remarkably fast to most alkaline treatments. A feature of the process is the relatively high loading that is required to give a flameproof fabric.

The more general method of modifying cellulose, the urea–formaldehyde crease-resist process, has little effect on flammability. The treated fabrics are not flameproof and ignite as readily as untreated fabrics, with only a small increase in char.

(*b*) Precipitation Methods

Application of certain metallic oxides produces a flameproof cellulose, although the treated material is not glowproof. The oxides are usually applied by a two-bath process which precipitates them in or on the cellulose. The treatment has some fastness to washing.

Probably the earliest precipitation method used commercially was the "Perkin" process[22]. An example of the process is as follows—

> The flannelette is run through a solution of sodium stannate at approximately 45°Tw. It is then squeezed to remove the excess of the solution, passed over heated copper drums in order to dry it thoroughly, after which it is run through a solution of ammonium sulphate of about 15°Tw. and again squeezed and dried. Apart from the precipitation of stannic oxide the material now contains sodium sulphate and this is removed by passage through water. The material is then dried.

This was considered to be a satisfactory treatment, but later research has shown that it is not fast to washing and that it causes serious tendering on exposure to light. The early claim of fastness to washing was probably due to the presence of occluded ammonium salt.

The latest examples of this type of treatment are Erifon (DuP)[23] and Titanox FR[24] (Titanium Pigment Corpn.).

Erifon is an acid solution of antimony and titanium oxychlorides. The treatment is carried out by padding the fabric through the solution, squeezing, passing through a 15% solution of sodium carbonate, rinsing thoroughly, and drying. The flameproofing results obtained on cellulose fabrics are good, although there is appreciable afterglow. The afterglow can be subdued to some extent by the addition of sodium silicate to the alkali bath.

It has been suggested[25] that a reaction takes place with the cellulose to form cellulose titanate, and that the antimony oxychloride reacts with this substance. If this is true, it should be possible to carry out the process without dulling the fabric, but in practice it is difficult to prevent surface precipitation, and if the fabric is dyed a dark colour the appearance is likely to be completely spoiled. Some improvement may be obtained by removing the excess of Erifon from the fabric by passage through a concentrated solution of sodium chloride before immersion in the alkali. Even with this modification, it is extremely difficult to produce a clean fabric, and the treatment in salt removes some of the flameproofing material which should be left in the fabric. An interesting sidelight on this treatment is that, although titanium oxide is precipitated within the fibre, photodegradation is not accelerated: in fact, the treatment appears to give some increase in tensile strength. This treatment is quite fast to washing.

Titanox FR is a very similar product to Erifon, but contains titanium dichlorodiacetate with antimony oxychloride. The foregoing remarks apply also to this product, and it has the added disadvantage that it is necessary partly to dry the fabric while it is still in an acid state. This is a difficult operation to perform without tendering the fabric.

(c) Coatings

Another method of fixing an oxide on the fabric is by means of a suitable resin. The application of a resinous matter plus an oxide is applicable only to coarse fabrics, because this type of treatment spoils the handle of fine materials. A large quantity of the flameproofing material is required, sometimes as much as 50%.

A good example of this type of treatment, developed in America during the war and modified here, was known as the *C.W.S. treatment*, and was used extensively for tentage and similar fabrics[26].

As originally formulated, this process used antimony oxide and Vinylite VYHH (Carbide & Carbon Chemical Corpn.) (vinyl chloride–acetate copolymer) applied from an organic solvent; if necessary, the fabric was soaped to reduce the stiffness. The process was modified in this laboratory by the addition of Cerechlor (ICI) to reduce the stiffness and of zinc oxide to reduce the serious afterglow. The afterglow could not be completely eliminated because, if too high a proportion of zinc oxide was added, the flameproofing properties of the mixture were destroyed.

Other modifications of the original formula have included the addition of calcium carbonate to neutralise any hydrochloric acid that may be formed during storage.

Later developments in this field include the production of materials in emulsion form, and products of this nature are now available commercially.

Flameproof Yarn

The modification of regenerated cellulose before spinning, so as to produce a flameproof yarn, has been suggested; it has been investigated to a limited extent, but without any commercial success to date.

According to Marvel and Bluestein[27] it is possible to make from partly acetylated cellulose a mixed cellulose ester containing phosphorus which is flameproof. The Celanese Corporation of America claim a somewhat similar type of material[28], produced by reaction of a bishalogenoalkyl chlorophosphonate with acetylated cellulose in pyridine solution, which results in cellulose acetate bis-2-chloroethyl phosphate. It is not known whether either of these processes could be used for the production of a satisfactory flameproof yarn. Both treatments would give thermoplastic yarn.

The addition of phosphorylamide (formed by reaction between phosphorus oxychloride and ammonia) to the viscose dope has recently been claimed to produce a flameproof yarn[29].

3. OTHER FIBRES AND THEIR TREATMENT

Cellulose Acetate

Cellulose acetate may appear to be less readily inflammable than cellulose, because it shrinks from the flame, but once it is ignited it burns readily, and molten drops fall away from it. These flaming drops may ignite other materials, so that in some circumstances cellulose acetate may be a greater fire hazard than cellulose.

A number of processes for flameproofing cellulose acetate plastics are available, but they depend upon the use of substances, such as phosphoric esters, which act as plasticisers and are therefore unsuitable for use in yarn in sufficient quantity to prevent flaming.

No very satisfactory method is available for the treatment of cellulose acetate textiles, which is made difficult by the low imbibition of the material.

Of the methods suggested most use expensive chemicals, e.g. ethylenediamine dihydrobromide[30].

A process patented many years ago by British Celanese Ltd. entails treatment of the fabric in 15% phosphoric acid followed by rinsing in water. The object of the process is no doubt to replace some acetyl groups by phosphoric acid. Trials do not suggest that it is very successful.

Some reduction in inflammability can be obtained by application of a 10% solution of ammonium thiocyanate, but since the treatment swells the fabric the strength is reduced.

Wool

Because of its much higher ignition point and the fact that on burning it forms a bulky ash, wool is not so great a fire hazard as cellulose and it is not normally flameproofed. Once it is ignited, however, it burns readily. It has been suggested that a suitable treatment is desirable.

Nylon

Although this fibre has not been regarded as a fire hazard because it melts before the flame, and tends to drip away after igniting, once ignited it burns readily, and serious burns can result from contact with the molten material. The flammability is increased by dyeing with metallised dyes such as the chrome dyes. A method of flameproofing using a thiourea resin has been suggested[31]. The effect of the usual flameproofing salts has been examined by Hasselstrom *et al.*[32], who claimed that use of ammonium sulphamate, thiourea, or thiourea–formaldehyde resins gave satisfactory results.

Fabrics made from a Mixture of Yarns

Mixtures of cellulosic yarns with other materials are difficult to treat. For example, the combination of the comparatively safe fibre, wool, with cotton or Fibro produces a relatively dangerous material; treatment with the usual flameproofing solutions such as borax–boric acid does not give a satisfactory result if the wool content is more than about 50%. Special treatments will have to be evolved for such fabrics.

An even more difficult material to treat is one composed of cellulose and cellulose acetate. One treatment which reduces the inflammability of this type of material, but which produces a rather damp fabric, consists of a mixture of potassium formate and ammonium dihydrogen phosphate.

Mixtures of cellulose or wool with the new fibres such as Orlon present similar difficulties.

4. A THEORY OF FLAMEPROOFING

In this discussion cellulose fibres, which are the most widely used of textile materials, will be

considered: the general principles emerging are applicable to all fibres.

Mechanism of Flame Propagation

Cellulose is a solid with negligible vapour pressure, heating to ca. 275°C. promotes a slightly exothermic reaction[33], by which the cellulose is decomposed into a carbonaceous char and volatile materials—mainly carbon monoxide, carbon dioxide, water vapour, and combustible tarry materials. At ca. 320°C. ignition takes place[34]. The combustion of the volatiles produces the flame, and that of the char causes the so-called afterglow.

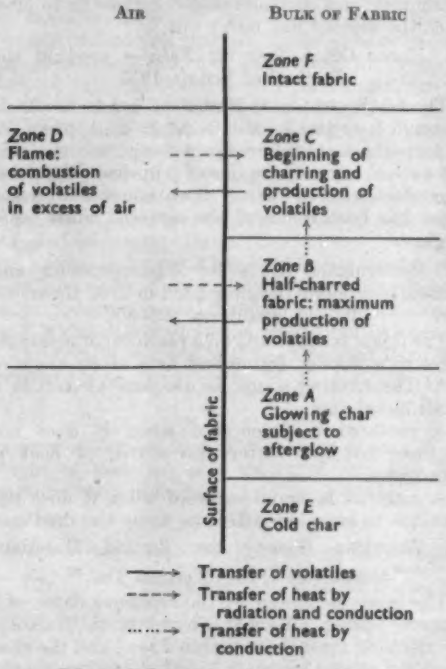


FIG. 1—Schematic Representation of Zones in a Vertically Burning Fabric

The steady propagation of a flame up a vertical strip of combustible fabric is a very complex process taking place in a complex system, and results from a number of interacting chemical and physical factors (Fig. 1). In the course of time all the zones will move steadily up the strip, so that Zone F (intact fabric) is encroached on by Zone C, and Zone B and Zone A move up progressively to increase the amount of cold char in Zone E. Radiation and conduction from Zone D (flame) must be great enough to produce sufficient new volatiles from Zones B and C to replace steadily the volatiles consumed in the flame. If this condition is not met, and the new volatiles are not sufficient to replace consumption, the flame will gradually go out, and the burning will cease to be propagated. It is of interest to apply the scheme to several special cases—

(*a*) Cellulose ceases to burn in an atmosphere containing less than ca. 10% of oxygen. In low-oxygen atmospheres, the area of Zone D (flame) increases, so that the energy received by unit area of Zones B and C is diminished; the glow reaction of Zone A is retarded, so that Zone B receives less energy by conduction; production of volatiles is slower, and the flame will not propagate in the steady state without application of an outside source of heat. Conversely, dynel (a copolymer of vinyl chloride and acrylonitrile) will not burn in air, but burns without difficulty in an atmosphere containing ca. 35% of oxygen.

(*b*) Fabrics of open structure or with a raised surface are more combustible than a compact fabric; a flameproofing treatment satisfactory on the last-named may not be fully effective on the former fabrics. Here the energy from Zone D is very effective, since every fibre in the structure receives its quota, with consequent rapid rise of temperature and production of volatiles.

It should be noted here that on ignition a pile fabric may flash with a surface burn, leaving the base fabric intact and unignited. The effects of energy on the pile and on the base fabrics are so different that one is combustible and the other non-propagating under the conditions of the flash.

(*c*) If the energy flux from Zone D is augmented by heat energy from an external source, then most so-called fireproofed textiles can be made to burn. This may be illustrated by citing fireproof curtains in a burning room: the curtains will burn and add the heat of their combustion to the total energy of the conflagration.

The thermoplastic fibres, e.g. nylon, as they shrink away from the flame, are generally rated as virtually uninflammable. However, these fibres have a considerable heat of combustion, and in the appropriate circumstances must be considered a fire risk.

Effect of Flameproofing Treatments

The object of a flameproofing treatment is to modify the course of decomposition in such a manner as (*a*) to produce a smaller amount of inflammable volatile materials, and in certain cases (*b*) to produce volatiles which burn with a less intense flame, owing to a greater content of carbon dioxide and water vapour.

The ideal treatment should clearly cause dehydration of the cellulose on heating, producing decomposition to carbon and water vapour—

$$(C_6H_{10}O_5)_x \rightarrow 5xH_2O + 6xC$$

It has been found, largely by empirical methods, that the application of certain salts, oxides, etc. brings this about, and various theories have been advanced to explain their actions. These include—(i) the retardant decomposes, forming large volumes of gases which prevent the oxidation of the cellulose, e.g. ammonium salts; (ii) the retardant fuses, forming an impervious layer, which again prevents the access of oxygen, e.g. borax–boric acid mixtures; (iii) the retardant conducts away heat so rapidly that the cellulose does not reach the ignition temperature; and (iv) the cellulose is dehydrated, e.g. by oxides, alkalis, or ammonium salts. Of these theories the fourth is the most probable, although the actual method is still open to argument.

One possibility is that the flameproofing material combines with the cellulose before the flame temperature is reached, forming a new substance with decomposition characteristics different from those of cellulose. This theory is substantiated by the following evidence.

Despite the difficulty of determining what occurs at and near flame temperature, it has been possible to demonstrate that at about 200°C. ammonium dihydrogen phosphate reacts with cellulose, forming cellulose phosphate, and that at a somewhat higher temperature ammonium sulphate acts likewise, forming cellulose sulphate. Both these substances are known to be flameproof. Similarly, it can be shown that other retardants combine, or at least associate themselves, with cellulose. Examples of these include the borax–boric acid mixture, sodium tungstate, zinc chloride, and calcium chloride. In the first two cases combination takes place with the cellulose at ordinary temperatures, for it can be shown[35] that crease-resistant properties, which depend on chemical combination with the cellulose, can be obtained by the use of borax–boric acid mixtures or sodium tungstate. It is probable that chelate compounds are formed with the cellulose.

In the case of the chlorides it is well known that both zinc and calcium chlorides associate with hydroxyl groups, and it can be assumed that complexes or basic salts are formed on drying.

Other retardants which are also known to react with cellulose include titanic salts[27] and some metal oxides, e.g. antimony pentoxide, which produces a cross-linkage and renders the treated material insoluble in cuprammonium solutions (unpublished work).

Thus it seems reasonable to assume that, for a chemical to act as a retardant, it must be capable of reacting with the cellulose, and this theory is confirmed by the fact that none of the usual retardants will flameproof cellulose acetate, which has few reactive groups.

Schuyten, Weaver, and Reid[36] suggest that the dehydration occurs catalytically through a Lewis acid–base interaction via a carbonium ion or carbanion mechanism. The two theories are not incompatible.

The char which remains after the cellulose has been destroyed by heat is primarily carbon, and it is the oxidation of this which produces afterglow.

When carbon is oxidised, two mechanisms are possible—

(i) $C + \frac{1}{2}O_2 \rightarrow CO \quad \Delta H = -26{\cdot}4$ kcal.

(ii) $C + O_2 \rightarrow CO_2 \quad \Delta H = -94{\cdot}4$ kcal.

It is suggested that a glow-retardant functions by affecting the course of the oxidation reaction so that the primary product is carbon monoxide rather than carbon dioxide. By this means the second reaction is suppressed, and insufficient heat is evolved at the carbon face to sustain the carbon in a state of incandescence.

The two best glow-retardants are boric acid and phosphoric acid, which probably act catalytically, as quite small quantities are effective. However, as these substances are retained very tenaciously by the char, some form of surface inactivation or actual combination with the carbon cannot be ruled out.

5. TESTING

Flameproof Tests

To be classed as flameproof a fabric must pass one of the standard tests. There are several of these, differing mainly in method of ignition and whether the fabric is held horizontally, vertically, or at an angle.

(*a*) British Standard *B.S.* 476 : 1932

The fabric is held at an angle of 45° and ignited from absolute alcohol burning in a small cup. The fabric must not continue to carry flame or to glow after the alcohol has burnt out.

(*b*) Home Office Test for Fabrics used in the Festival of Britain 1951

The fabric sample, at least 2 ft. × 1 ft. in size, is suspended vertically and a taper is applied for 30 sec. The material must not flame, and charring not extend beyond a radius of 5 in. from the point of contact with the flame. Two minutes after the taper has been removed the material must cease to glow.

(*c*) Performance Tests for Flameproofing and Smoulder-proofing recommended in *B.S. Handbook* No. 11 (1949), pp. 305–307

The fabric is supported on a platform of nichrome wires in a wooden frame and held at an angle of 45°. The igniting source is absolute alcohol in a small metal cup.

A material is flameproof when it does not continue to flame after the source of heat is withdrawn.

A material is smoulder-proof when it does not continue to smoulder after the flame has died out.

(*d*) American Society for Testing Materials, Committee D 13— Vertical Test[37]

The fabric is ignited by the luminous flame of a Bunsen burner. To be considered satisfactory, afterflaming must cease within 2 sec., and the char must not exceed a certain length depending on the weight of the fabric.

Flammability Tests

Some idea of the flammability of a fabric can be obtained by determining the rate at which it will burn. This aspect of testing fabrics has been studied extensively in America, resulting in the production of the AATCC flammability tester. In this country, the main recent developments have been a "semicircular test apparatus" and an apparatus for measuring the vertical burning rate.

(*a*) AATCC Flammability Tester[38]

A brief description of the machine and the test is given below. Ignition is by a standard butane flame $\frac{3}{4}$ in. long applied to the fabric for 1 sec. by a mechanism which simultaneously sets in motion a stop-watch. The pattern, 6 in. × 2 in., is placed at an angle of 45° in a special holder within a draught-proof chamber. A cotton thread is stretched across the pattern 5 in. above the point at which the flame is applied. When the flame from the burning fabric severs this thread the watch is stopped automatically.

By the U.S. Flammable Fabrics Act, as amended, an oven-dry unraised fabric which takes longer than 3·5 sec. to sever the thread is classed as of normal flammability (Class I).

(*b*) Semicircular Tester[39]

In this test a strip of fabric 21 in. × 1½ in. is clamped round a semicircular frame, and the fabric is ignited by means of an alcohol flame. The distance or the time or both are measured.

(*c*) Apparatus for determining Vertical Burning Rate

This test involves the measurement of the rate of loss of weight of a burning strip and was evolved by the Fire Research Station, Boreham Wood. The instrument was specially designed to overcome the difficulties inherent in a test for vertical burning rate. It consists of a torsion balance to which a mirror is attached at the fulcrum. A beam of light is directed at the mirror and focussed on a strip of photographic paper attached to a revolving drum. The strip of material to be tested is suspended from the end of the balance arm and ignited. As it burns the loss of weight is recorded photographically.

A similar instrument has been constructed in our own laboratory, in which, however, recording is made direct on paper, fitted to a revolving drum, by a stylus attached to the end of the balance.

The rate of burning is then calculated from the formula—

$$\frac{rl}{W-w}$$

where r = rate of loss of weight in g/.sec., W = weight of material, w = weight of ash, and l = length of strip in inches.

TABLE I

Fabric Composition	Fabric Weight (oz./sq.yd.)	Burning Rate (in./sec.)
Viscose rayon staple	3·5	2·5
	5·5	1·8
	8·5	1·0
Cotton	2·0	5·0
	5·0	1·9
	7·3	1·6
Wool	8·0	0·8
Cellulose acetate	8	0·8
Wool–cotton (50 : 50) ...	10	1·1
Wool–Orlon (50 : 50)	8·5	1·4
Viscose rayon staple–Orlon (50 : 50)	11	1·8
Viscose rayon staple–Dacron (50 : 50)	11	1·1

Some interesting results have been obtained, of which a few are given in Table I. The dimensions of the strips used were 1½ in. × 3 ft.

Determination of Temperature of Ignition

The difficulty of determining the true ignition point of fabrics is well known, yet this factor is important in the determination of fire hazard.

(*a*) Taylor and Pollok[40] have described a method in which they placed the sample on a silica plate heated in a hot-air bath. The sample was kept in contact with the plate by the bulbs of four thermometers held vertically. By this means a temperature of ignition for filter paper of ca. 340°C. was obtained.

Similar experiments have been carried out in our own laboratory but using a brass plate to which was brazed a thermocouple. The figures obtained were much higher than the ones quoted, and depended to some extent on the size of the pattern used. They demonstrated, however, that the ignition point of cellulose fabric was appreciably lower than that of cellulose acetate, nylon, Terylene, or wool.

(*b*) In another method, designed in our laboratory primarily for the comparison of the ignition point of fibre webs, short lengths of web are drawn across an electric element. The temperature of the element is altered by adjusting the current passing through it by means of a Variac transformer and is measured by means of an optical pyrometer. Table II gives typical results obtained on Scotch Feed webs about 4 in. wide, weighing 2·5–3·0 g./ft. (ca. 0·1 oz./ft.).

TABLE II

Composition of Web	Ignition Point (°C.)
Ardil (3·5 denier, 2½ in.) unbleached	870
Fibrolane (3·5 denier, 2½ in.) ...	870
Wool 64s noils	890
Cotton (Tanguis)	700
Fibro (3 denier, 2½ in.)	690

(*c*) Experiments in which the source of ignition was radiant heat have been carried out using a machine designed by the author.

The machine consists essentially of (*a*) a U-shaped electric heating element, the current in which is controlled by a Variac transformer, and (*b*) a fabric-holder mounted on a carriage so that it can be placed rapidly between the limbs of the element. The temperature is measured by means of a thermocouple placed between the limbs at a point close to the edge of the fabric.

The time taken at different temperatures for the fabric to ignite, or for flameless combustion to commence, was measured. The experiments are not yet complete, but some interesting results have been obtained.

It has been found, for example, that the time of ignition at any given temperature varies with the weight and the construction of the fabric; and that the application of weak solutions of flameproofing salts tends to increase the speed of ignition, although flameless combustion is prevented at low energy input.

These experiments also showed the importance of taking into account the source of heat when determining fire hazard. A good example of this is provided when the fire hazards of a heavy cotton canvas and a thin net are compared. If a flame is applied to these fabrics it is obvious that the net is more flammable; however, if they are placed in front of an electric heater under suitable conditions, the canvas may be ignited when the net is merely scorched.

Discussion of Tests

Only a few of the recognised tests have been detailed above, but enough to show that there is a lack of agreement on the best methods of test. This is largely due to the difficulty of defining a flameproof material. Without an absolute definition the various tests are, at best, arbitrary standards, suffering from the disadvantage that a material classed as flameproof may support its own combustion if the conditions are sufficiently severe, e.g. when placed in a roaring Bunsen flame. Thus even a "flameproof" fabric may constitute a limited fire hazard.

Thus to cover all aspects of fire hazard additional methods of test are required. These could well include determination of the speed and the temperature of ignition (using radiant heat as well as a naked flame) and of the amounts of heat and char produced on combustion. The importance of these properties can be illustrated by the behaviour of wool, which is much less of a fire hazard than cellulose, primarily because it has a much higher temperature of ignition and forms a considerable quantity of char on burning.

Some treatments may affect the various factors in fire hazard to different degrees, as, for example, treatment of a cellulose fabric with 2-3% ammonium phosphate. This will reduce the burning rate by ca. 40% and increase the char (nil in the untreated fabric) to 20–25%, with a consequent reduction in the amount of volatile combustible material; it will also allow the burning fabric to be more readily extinguished. On the other hand, the treated fabric is more readily ignited by radiant heat.

Obviously, it is desirable in the determination of fire hazard to assess the relative importance of (i) ease of ignition, (ii) rate of burning, and possibly (iii) ease of extinction of the flame.

None of the standard tests are really satisfactory for all purposes. They are not particularly suited, for example, to the testing of thermoplastic fibres, such as cellulose acetate, nylon, etc., which melt before the flame or radiant heat. A suitable test for these fibres has yet to be devised.

For some materials, also, the tests bear little relation to the actual conditions of use; e.g. they are unsuitable for determining the fire hazard of carpets, which may burn readily when held vertically and yet may not be capable of ignition when laid on a floor.

6. GENERAL REMARKS

The passing of the United States Flammability Bill and prospective legislation in New Zealand demonstrate the increasing awareness of the risks involved in the sale of dangerously flammable textiles for clothing. This should further stimulate research into the production of materials with reduced fire hazard.

Temporary methods of attaining this are well known but are unsuitable for materials which have to be cleaned repeatedly: a treatment is required which will render the textile flameproof throughout its useful life. Considerable success has been achieved, but further research is required to produce a completely satisfactory commercial process.

Further work on the determination of fire hazard seems desirable, and an effort should be made to attain greater unanimity on the definition of a "flameproof" fabric.

Finally, tests and acceptance standards should be related in some way to the conditions of use of the material: whether this is possible is problematic; that it is eminently desirable is obvious.

* * *

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TEXTILE RESEARCH LABORATORY
COURTAULDS LTD.
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Cellulose Acetate and Water Repellency

R. J. MANN

Meeting of the London Section held in the rooms of the Royal Society, Burlington House, London W.1, on 7th January 1955, Mr. R. A. McFarlane in the chair

The methods in use for making fabric water-repellent and the methods of measuring these properties are briefly reviewed. Experiments are described to determine the best available method for increasing the water-repellency of cellulose acetate, special attention being given to the silicones on account of their superior properties and comparative unfamiliarity.

(a) Relation of Cellulose Acetate to Other Fibres

Twenty years ago cellulose acetate would have been described as a hydrophobic material in its own right. In comparison with the then current textile materials it was unique (with the possible exception of silk) in its small affinity for water, and this property was responsible, until experience was gained in its handling, for some troubles in the dyehouse.

Nowadays, however, cellulose acetate ranks between the older fibres and the modern synthetic materials in its water imbibition properties, as is shown by Table I, compiled from various sources [1–4].

TABLE I

Water Imbibition of Various Fibres
(c.c. of water absorbed per 100 g. of fabric)

Fibre	(1)	(2)	(3)	(4)
Viscose rayon ...	103–66	45–75	85–100	104–134
Cellulose acetate	31–22	16	35	28
Cotton	48	35	—	42–46
Linen	55	—	—	46
Wool	49	35–40	—	39–42
Silk	22–54	—	33	33
Nylon	17	10	13	13
Glass	13·5	—	—	—
Vinyon	7	—	—	11
Terylene (ICI) ...	5	—	—	7

The considerable differences in the figures quoted for a given fibre correspond with different procedures adopted in their determination, but in all cases it can be seen that cellulose acetate is consistently less hydrophilic than the natural fibres except silk, and less hydrophobic than the newer synthetic fibres.

Whilst hydrophobicity of a fibre makes for only slight swelling on immersion in water and consequently impedes dyeing by the older methods, there are many applications in which a hydrophobic fibre is of great use. No-one who has lived in England during the summer of 1954 will dispute that a really water-repellent covering can be invaluable. Such materials are generally classified as *waterproof* or *showerproof*. In the trade a "waterproof" material is understood to mean one which, by virtue of a continuous film, e.g. of rubber or plastics, is made capable of supporting a pool of water indefinitely so long as its structure remains unimpaired. Such a material, besides being waterproof, is ventilation-proof and is uncomfortable to wear for long periods.

Those who had experience, during the 1939–1945 war, of the use of oilskin anti-gas protection will remember the intense discomfort caused by the inability of perspiration to disperse. So distressing and fatiguing was it that tours of duty under these "hermetically sealed" conditions were limited to very short periods. Whilst such severe conditions are not, of course, met in normal daily life, it is clear that any garment which impedes loss of perspiration is undesirable if its virtues can be achieved in other ways.

A *showerproof* fabric, on the other hand, is porous and permits "breathing". Consequently it allows escape of perspiration, and is comfortable in wear indefinitely. Whilst unsuitable for heavy storms, such materials are ideal for summer showers, and can be daintily constructed in attractive colours and materials. They can be light and easily packed into small space, or of any desired weight to suit the purpose in hand and the purse of the wearer. They owe their effectiveness to the inherent water-repellency imparted to the actual fibres by the application of suitable finishing agents. As they are truly water-repellent, splashes of ink, soup, and other liquids can be quickly shaken off and rinsed clear.

(b) Methods of Testing

Tests of showerproofing efficiency are numerous, but fall into the following main groups—

(i) Those depending on the time taken visibly to wet the surface of the material being tested, e.g. Rille test, spray rating test

(ii) Those in which penetration of the material is the index of efficiency, e.g. hydrostatic head test, drop test

(iii) Those depending on the amount of water absorbed by the fabric under standard test conditions, as referred to in Table I but not commonly used for commercial testing

(iv) Combinations of two or more of the above principles, e.g. Bundesmann.

RILLE OR TROUGH TEST—This is an ingenious method used by the IG. Farbenindustrie AG.[5]. Descriptions of this method vary in detail, but the principle is to arrange a half-round channel 4 cm. in diameter and about 25 cm. in length at about 20° to the horizontal. A specimen of the fabric under test is supported by means of a clamp at the upper end of the channel, and water coloured with a dilute solution of eosin or other dye is dropped at the rate of 150 drops per minute on to the

clamp, whence it runs down the channel. The drops at first retain their separate identities (often referred to as "pearling"), but as the surface of the fabric becomes wetted they join to form a continuous stream, and the time necessary for this to occur is taken as the measure of the water-repellency of the sample. This ingenious method takes account only of the water-repellency imparted by the treatment, but does not measure the serviceability of the treated fabric.

SPRAY RATING TEST—This test is largely used in America and has some value as a measure of serviceability, since both force of impact and wettability are concerned in the quoted value. One method of carrying out this test has been described by the Unification of Testing Methods Committee of the Textile Institute [6]—

A standard-sized cutting of the fabric under test is mounted in a frame and arranged at 45° to the horizontal. Six inches above the centre of the sample is fixed a multi-perforated jet of specified characteristics (number of holes, their size and spacing), and this is connected above with a funnel. The test is carried out by pouring into the funnel 250 ml. of water, which falls as a spray on to the inclined sample. When the flow is completed, the sample is removed in its frame, tapped in a specified manner to remove lightly adhering water, and then graded according to a visual assessment of surface wetting. If the surface of the fabric is completely unwetted, it is rated 100, and correspondingly smaller values, at 10-unit intervals, are given according to the degree of wetting.

This method makes a reasonable, if somewhat rough, attempt to assess serviceability, but is too subjective and not sufficiently discriminating for investigation purposes.

HYDROSTATIC HEAD METHOD—A simple apparatus for this commonly used method is shown diagrammatically in Fig. 1. The fabric under test is stretched tautly over the funnel *A*. Water is run at a standard rate into the calibrated tube *C*. Since the fabric is porous, the air in the system escapes through it until the water in both tube *C* and funnel *A* reaches the level of the fabric. Further addition of water to tube *C* results in the build-up of a column of water in the tube, and this continues until the pressure becomes sufficient to force the water through the fabric. For a given fabric, the more water-repellent the material the higher the column will rise, and the height at the first sign of penetration or the maximum height of rise may be taken as a measure of the water-repellency of the fabric of the diaphragm.

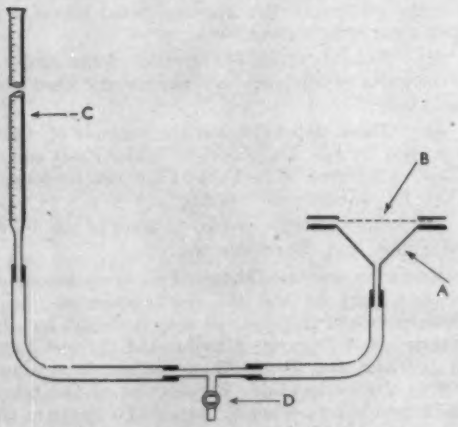


FIG. 1—Hydrostatic Head Method

This method tends to lay undue emphasis on the pressure aspect of water-repellency without much straightforward relation to conditions of use, and since it depends on penetration of the fabric by water under pressure, flaws in the fabric or irregularities due to handling can affect very considerably the result obtained.

DROPPING TESTS have been proposed from time to time, one such being to support the fabric to be tested on a frame set at 45° to the horizontal and to drop water from a stipulated height at a stipulated rate—18 drops per minute from a height of 6 ft. has been recommended, the drops being of known size. Alternatively, 60 drops per minute from a height of 4½ ft. has been recommended [7]. The value given for the showerproofing of the material is the number of drops (or the time in minutes) before penetration occurs. To aid the determination of this time, a backing of coloured blotting paper can be used. Such a test is, of course, a very arbitrary one and does not measure serviceability. A very open fabric will permit the first drop to pass through it whether an efficient water-repellent treatment has been applied or not; and the continual dropping on to one spot does not simulate actual conditions of use. The effect of the proofing treatment thus influences the result obtained only in an indirect way.

BUNDESMANN TEST—It is, in fact, generally agreed amongst investigators in this field that no universally satisfactory test for water-repellency exists. Much depends on the use to which the fabric under test is to be put. In this country, it is considered that, for testing of fabrics to be used as "showerproof" apparel, the best test is the Bundesmann. This method takes account of both penetrability and absorption, and both figures are obtained under conditions which simulate reasonably well the conditions likely to be encountered in use. The samples are exposed to a scattered shower falling at a specified rate, and a special device scrapes the underside of the sample in an attempt to imitate the rubbing to which a raincoat, for instance, would be subjected in wear. Means are provided for catching the water penetrating the sample, and the water absorbed by a standard area of fabric is determined by weighing. Details of the construction of this machine were published in the *Journal* in 1943 [8].

Providing that the machine is well maintained, it gives a reasonable method for comparing different samples, but much remains to be done in

TABLE II

Bundesmann Machine for Testing Water-repellency
Comparison of Results from Different Machines

(Increase in wt. (%) and penetration (c.c.))

Sample	Laboratory A				Laboratory B							
	1st Test		2nd Test		1st Test		2nd Test		3rd Test		4th Test	
	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)
I	28·3	9·0	29·4	10	33	30	35	27	36	21	39	28
I	—	—	—	—	34	16	40	18	39	14	39	16
II	26·2	1·0	35·5	2·0	33	3	38	2	35	2	36	2
II	—	—	—	—	35	2	37	1	34	1	35	2
III	46·2	7	45·8	7	18	7	19	8	20	7	23	7
III	—	—	—	—	19	8	28	7	24	8	24	9

standardising details of construction and usage before absolute figures can be given which can be repeated on different machines and under the conditions of different laboratories.

This is illustrated by Table II, which shows values obtained in different laboratories on the same set of materials. It is clear from these figures that great care must be taken to ensure standardised conditions and that, given such standardisation and careful working, a laboratory can achieve reasonably repeatable results. It is obviously desirable, as in all tests of fabrics, to take the mean of several determinations. We normally make two determinations (as in Table II), and if these are in good agreement accept them; otherwise a further two determinations are made and the mean is taken.

For much of our early work no Bundesmann machine was available, and our tests were made by the hydrostatic head method. When our first trials were made on a Bundesmann, using fabrics for which results had previously been found by the hydrostatic head method, we were amazed at the way in which the samples were sorted out. Fabrics which had previously been considered good for water-repellency were immediately thrown out, by simple inspection during the test, as quite hopeless. Table III shows readings obtained by five methods.

It is considered that any fabric which has a pick-up figure when tested on the Bundesmann of 50% and a penetration figure not exceeding 10 c.c. is very good.

These figures show that, except in the case of cotton by the hydrostatic head test, all methods used agree in picking out the best and worst of a fairly widely separated series; but that there can be considerable disagreement when it comes to distinguishing finer differences. In the case of the cotton fabric, indeed, there are some blatant discrepancies. For instance, the spray rating of cotton processed by methods 1 and 3 is identical, but this is completely belied by the drop test, the Rille test, and the Bundesmann. Again, the drop test and the hydrostatic head test put methods 3 and 4 in the same category, but all other tests show that method 3 is superior to method 4.

As mentioned above, in spite of its manifest imperfections, the Bundesmann appears to be the best method for testing the showerproofing of fabrics intended for apparel, and this method is generally adopted in results quoted in this paper.

One further point should be noted before leaving the subject of testing. Most materials are liable at some time during their useful life to be cleaned in some manner. According to the type of fabric and the use to which it is put, this may be either a

TABLE III

Water-repellency Values by Different Test Methods

Process	Bundesmann (%)	Bundesmann (c.c.)	Hydrostatic Head (cm. upheld)	Spray Rating	Rille Test	Drop Test
			ACETATE RAYON TAFFETA			
1	34·5	1·8	24·7	100	26 min.	360
2	36	83	17·7	80–90	10 sec.	39
3	60	10·5	22·1	90–100	30 sec.	315
4	63	20	20·3	80–90	10 sec.	296
5	128	111	8·5	50	0	19
6	87	—	13·9	80	0	37
			COTTON NAINSBETTER			
1	22·5	1	30·1	100	25 min.	143
2	106	240	37·2	70	0	8
3	90	19	38·7	100	8·5 min.	17
4	115	157	36·2	80	50 sec.	19
5	136	161	15·5	70	0	26
6	96	29	34·7	90	2 min.	32

washing with aqueous soap or other detergent or a dry cleaning with one of the usual dry-cleaning solvents. It is therefore desirable that, for the highest-quality work, the proofing should be fast to such treatments, and most of the results quoted later in this paper will include figures showing fastness to scouring and to dry cleaning. The tests used in the examples quoted are—

(1) Washing in soap (5 g./litre) at a liquor ratio of 50 : 1, stirred by hand for 15 min. at 60°C.

(2) Dry cleaning by immersion for 15 min. with gentle hand movement in tetrachloroethylene (perchlorethylene) at room temperature and at a liquor ratio of 30 : 1. The operation is then repeated in fresh perchlorethylene.

A single treatment on these lines is often sufficient to differentiate between two processes, but for final assessment, and before being able confidently to certify good fastness, these tests should be repeated up to at least six times with intermediate drying.

Tightly woven fabrics such as taffetas are easily creased and distorted, and such mechanical damage can seriously affect apparent water-repellency. For this reason, although not strictly a fair imitation of conditions actually used in such operation in the normal course of usage, the dry-cleaning tests have been carried out on the fabric in a flat condition.

(c) Methods for Producing Water-repellency

A very extensive patent literature covers a considerable variety of treatments.

WAXES AND SOAPS

Most of these methods depend on the use, somewhere in the process, of aliphatic compounds with chains of about 16 carbon atoms or upwards. Paraffin wax is a common starting point for many preparations, and various methods are described for producing emulsions of waxes and for making such emulsions stable to the conditions of application. Metal salts are often used in conjunction with such emulsions, and there are on the market numerous proprietary materials, for one- or two-bath applications, in which these methods are used.

The finisher of materials for the modern textile market is expected to have available special finishes to meet all occasions and requirements. These special finishes must be produced without any adverse effects on other properties, and in applying water-repellent finishes the finisher must exercise great caution to ensure that, for instance, light fastness is not reduced below the value considered necessary for the type of material being treated. Cellulose acetate is liable under adverse conditions of storage, or if not dyed with resistant dyes or suitably protected, to suffer from gas-fume fading, and care must be taken to avoid any materials which have a serious effect on this property. If they cannot be avoided, steps must be taken to rectify the fault by further special treatment. Further reference to these points will be made in the course of this paper.

One of the earliest processes by which the hydrophobic properties of the long aliphatic chain were exploited was the use of insoluble soaps. Probably the most commonly used was an aluminium soap, which was generally precipitated on the fibre by a two-bath process. This in turn was a development of the still earlier methods which depended on the hydrophobing properties of basic aluminium salts precipitated in or on the fibres. The fabric is first impregnated with a soluble sodium soap, by immersion and hydro-extraction, or by padding, and then passed through a bath containing an aluminium salt.

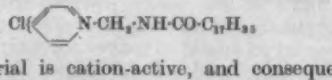
In recent years, the use of zirconium salts has been recommended. Thus the National Lead Co. (U.S.A.) have patented [9] a process in which zirconium in the form of ammonium zirconyl carbonate is used mixed with a soluble soap in a single bath. The colloidal solution thus produced is claimed to be stable at room temperature for several hours, but to form the insoluble zirconium soap on warming to 60°C.

Long-chain fatty compounds such as waxes can be applied, by those finishers who have the facilities, from organic-solvent solution, but for the sake of economy, means for recovering the solvent are necessary, and can be justified only when considerable bulk is to be processed. Fire risks and toxicity may also be serious considerations. When applied from a solvent, waxes are readily removed by similar means, and consequently the water-repellency produced is not fast to dry cleaning.

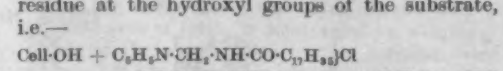
VELAN PF

A very great advance was made by Imperial Chemical Industries Ltd. when Velan PF was introduced in 1937, since this was the first of a new type of reagent which, by suitable treatment, could be made to combine chemically with the fibre.

As is well known, Velan PF is a quaternary ammonium compound believed to be stearamidomethylpyridinium chloride [10] and to have the constitution—



This material is cation-active, and consequently has some affinity for most textile fibres, which possess a negative charge. This affinity is not in itself, however, sufficiently great to result in a chemical combination with the substance of the fibre, and combination is believed to occur when the impregnated and dried material is subjected to a suitable heating treatment. This baking results in the splitting off of pyridine from the Velan molecule, and is thought to result simultaneously in the combination of the long-chain residue at the hydroxyl groups of the substrate, i.e.—



If this is a true picture of what happens during the treatment of cellulose with Velan, it is to be expected that cellulose acetate would react less

effectively with Velan, since it has, on the average, only 2/9 of the number of hydroxyl groups possessed by cellulose. Nevertheless, probably owing in part to the inherent hydrophobic properties of the cellulose acetate itself, an effective water-repellency can be imparted to this fibre by Velan. Such treatment has the further effect of conferring an extremely soft handle, and in this respect differs very markedly from the finishes in which a metallic soap forms the basis of the treatment.

Other products which appear to be of similar constitution to Velan are the American Zelan (DuP) and the Swiss Cerol WB (S).

SYNTHETIC RESINS

In these days of plastics and synthetic resins, when the urea–formaldehyde crease-resist process is well established and numerous other applications of these and similar products are well known, it is not surprising to find that attempts have been made to fix long-chain compounds by means of such resins. There are, in fact, a few such materials on the market, notably the Phobotexes (Ciba) and Resin BT 320 (Beetle Products Co. Ltd.).

Our trials with this type of product were initially tested by the hydrostatic head method and gave the remarkably good figures shown in Table IV.

TABLE IV

Water-repellency of Fabric treated with Beetle Resin BT 320

(cm. water supported)

Fabric	As finished	After Dry-cleaning	After Washing
Acetate–viscose rayon staple	21·8	20·4	19·8
Acetate rayon taffeta ...	18·8	16·8	16·2
Light acetate rayon satin	19·0	18·0	17·5
Acetate rayon sharkskin	18·5	18·0	18·5

Subsequent tests on the Bundesmann machine, however, were much less encouraging in the degree of proofing obtained, but the particular material used for these trials has the very useful property of conferring some protection against gas-fading. As regards the effect on other properties, our tests show that the light fastness of disperse dyes is not adversely affected, but that if direct cotton dyes are to be used, as for example in blends, care must be taken to select only those dyes which are not affected in light fastness.

The bath is very simply and conveniently prepared. Considering e.g. the instructions given for the preparation of Beetle Resin BT 320, the requisite quantity of resin is pasted with a small volume of water at 40°C. and then let down to a thin cream. This is strained and diluted with water at 30°C. to about nine times the weight of the original resin. An amount of catalyst, AC 77, equal to one-tenth of the weight of resin, is separately dissolved in water at 35°C., ammonia being added to give pH 8·0, and then added to the diluted resin, making up the final amount to ten times the weight of resin. The fabric is impregnated, by padding or by other means, with this emulsion, dried, and stoved for e.g. 5 min. at 150°C.

SILICONES

The silicones have recently come into considerable prominence as water-repellents. Based on the pioneering work of Kipping, these materials have been developed chiefly by the Dow Corning Corpn. and the General Electric Co. in America, and initially their products were the only ones of the kind available in this country. Several other American firms have since taken up their manufacture, notably the Arkansas Co. Inc., the Continental Chemical Co., and the Onyx Oil & Chemical Co. Now, however, the British firm of Midland Silicones Ltd. has undertaken their manufacture, and markets silicone-based products for many purposes, including at least three water-repellents for use on textiles. It is understood that at least one other firm is likely, in the near future, to be in a position to supply such materials.

The skeleton of those silicones which are used as water-repellents consists of a chain of alternating silicon and oxygen atoms, thus—

$$-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-$$

The free valencies of the silicon are satisfied by normal carbon-based organic radicals, which may be varied almost indefinitely.

Our trials have been mostly concerned with the three Midland Silicones products known respectively as Drisils 104, 115, and 148, on account of their British origin and general satisfactoriness. The two first mentioned are sent out in the form of solutions in organic solvents, 104 in methylene chloride and 115 in white spirit, and both contain 65% silicones. These solutions are emulsified with the assistance of cetyldimethylammonium chloride (CDMBAC) or of Silicone Emulsifier 100 (SE 100). Our earlier trials made use of Drisil 104, but latterly, on account of early difficulties which could probably, with present experience, now be overcome, we have changed to the use of Drisil 115.

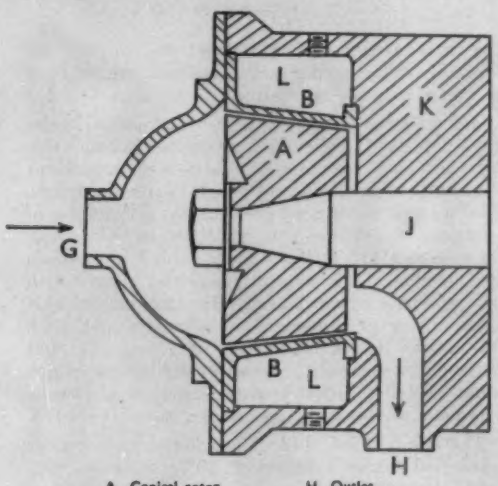
The third Drisil, 148, is marketed in a ready-emulsified form containing 40% silicones, 5% tetrachloroethylene, and 5% toluene, and this, as will be shown, tremendously simplifies the use of these materials.

The suppliers lay great emphasis on the need for very thorough homogenisation of the emulsions, and our trials confirm this. In our early trials on the laboratory scale using a small hand homogeniser, we were unable satisfactorily to emulsify with CDMBAC as recommended but appeared to be getting satisfactory emulsions when using an alternative emulsifier. We did a considerable amount of work with them, only to find when we commenced the treatment on a larger scale that the emulsions were unstable under bulk conditions. We therefore had to go back to the laboratory and look further into this matter of emulsification.

We then found that our earlier emulsions, using CDMBAC as the emulsifying agent and a small hand homogeniser, contained about 60% of

particles between 3 and 5μ. and 40% between 5 and 8μ., with occasional larger particles. We also found that by more thorough treatment we could get 90% of particles in the emulsion to a size of 2–3μ. with the balance between 3 and 5μ. These latter emulsions were considerably more stable, and under proper conditions could give satisfactory bath stability on the bulk scale.

Any who are interested in the preparation of these emulsions are referred to the literature published by Midland Silicones, and attention is drawn to the need for following very closely the recommendations given in respect of mechanical equipment. The first stage in the preparation of the emulsions from either Drisil 104 or 115 involves the formation of a thick water-in-oil emulsion by means of a high-speed stirrer. This is done by dissolving the dispersing agent in a small quantity of water and stirring vigorously whilst the Drisil is slowly added, followed by the balance of the water to give a final silicone concentration of 40%. We have found that a machine of the egg-whisk type is suitable for this purpose, the actual machine which we have used being made by Morton & Co. of Wishaw, Scotland.



A Conical rotor H Outlet
B Stator J Shaft
G Inlet L Water jacket

FIG. 2—Hurrell Colloid Mill

It is then most important to pass this initial emulsion through a colloid mill, possibly two or more times. We have found a Hurrell mill of the type shown diagrammatically in Fig. 2 to be very satisfactory. This operation must not, on any account, be skimped, and we have found it desirable to pass the emulsion up to four times through the mill. It is not a long operation, and such repetition is an excellent insurance against breakdown of the bath at a later stage—a very disastrous event. A point which should be noted here is the need for scrupulous cleanliness in all apparatus to be used for silicone processing. The silicone oils have an uncanny knack of loosening foreign matter of all kinds including oil and rust particles. The latter appear to form centres of activity about which oil spots form. It is easy to ensure that mangles are clean, but machines like colloid mills cannot easily be examined internally, and must consequently be thoroughly scoured by passage of copious quantities of soap solution and rinsed well with clean water. If any rust is left in the pipes, this will be loosened by the silicone and must be quickly filtered off.

It is recommended that Drisils 104 and 115 should be let down to a concentration in the master emulsion of 40% silicones when emulsifying with CDMBAC or to 25% silicones when using SE 100, and it is important that the pH of this emulsion should be right—not above 6 if using CDMBAC, and not less than 8 nor much above 9 when using SE 100.

The somewhat protracted and not entirely foolproof procedure involved in preparing one's own emulsion can be avoided by the use of the ready emulsified Drisil 148. It appears that certain metallic salts can be used as catalysts in the condensation which occurs at the later (curing) stage, and for this purpose Midland Silicones recommend the use with Drisil 148 of a substance which they call Catalyst N 16. It is mixed in the proportion of 1 part to 5 parts of Drisil 148, and simply diluted to working strength. The working strength will vary with the expression of the mangle used for its application, but it is generally sufficient to allow for a final pick-up of about 1·5–2% silicones. This should, however, only be taken as a rough guide, to be confirmed or modified as required for individual fabrics. Catalyst N 16 should not be used with Drisils 104 and 115.

It is, however, possible for those having suitable equipment to apply Drisils 104 and 115 from an organic-solvent solution, and in this case additions of certain organic compounds of zinc are recommended as catalysts.

Whichever silicone is used, it must be cured after drying to complete the condensation, so obtaining better and more permanent effects. Curing is carried out by heating at a temperature depending on the time of exposure. We have found 10 min. at 150°C. to be satisfactory.

It is also possible to use zinc with Drisil 115 by adding to the prepared emulsion, with CDMBAC, zinc acetate to give a concentration of 1 g./litre. This has the very useful effect of preventing the depressing effect which may otherwise occur on the gas-fading resistance of acetate rayon, particularly when using CDMBAC.

It is true that traces of dyebath assistants which may not have been completely removed during the final washing off may reduce the final water-repellency achieved. But we believe that the greatest danger of such foreign matter is that the bath may be thrown out of condition, causing accumulation of oily globules on the surface. These globules will be picked up by the fabric and will produce oil spots. If they are discovered at this stage, before curing has caused the final condensation to an insoluble resin, there is a reasonable chance that they may be removed by

thorough scouring or dry-cleaning. But once stoving has been carried out, there is no method we know of removing them without using materials which we consider too dangerous to the operatives. It is therefore of prime importance that fabrics should be examined, and re-treated if necessary, immediately after the padding and before the final stoving.

(d) Assessment of Various Processes

(i) COMPARISON OF DIFFERENT METHODS

For the purpose of assessing the relative values of the various types of treatment for high-class water-repellent acetate rayon fabrics we have compared, on the same fabrics, typical examples of the various materials described above. It is emphasised that we were searching for a material and a process which would give a good water-repellency which should not be unduly affected by dry-cleaning or by scouring; and that whilst some of the materials tested inevitably fall below this standard, they are still very valuable finishing agents in their own limited spheres and often have the advantage of lower costs both for material and for application.

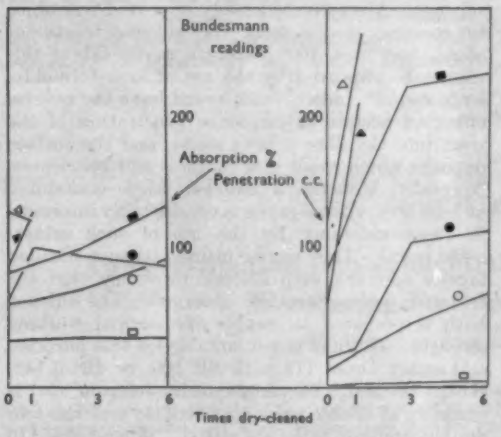


FIG. 3—Fastness of Water-repellency of Acetate Rayon Taffeta to Dry-cleaning with Tetrachloroethylene

Fig. 3 and 4 show the results obtained with six different agents. They show that the silicone method gives not only the best initial figures by the Bundesmann test but also by far the best retention of these properties after dry-cleaning with tetrachloroethylene and after scouring. Beetle Resin BT 320 and Phobotex both give comparatively good initial results, but these fall off somewhat more rapidly on dry-cleaning. The silicone treatment is similarly resistant to dry cleaning with trichloroethylene.

For these reasons, and because the silicones are of more recent introduction and require special care in preparation and application, further remarks are confined almost entirely to these materials.

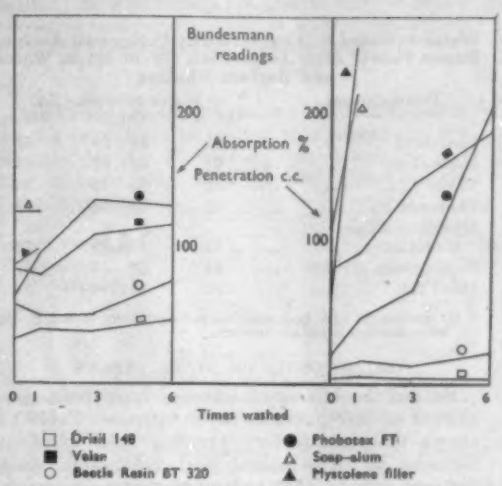


FIG. 4—Fastness of Water-repellency of Acetate Rayon Taffeta to Washing

(ii) EFFECT OF MECHANICAL FINISHES

It might be expected that a test which involves the bombardment of the fabric with water dropped from a considerable height would show benefit from mechanical treatments which result in consolidation. Results of trials intended to check this point have been rather inconsistent. In some cases a slight improvement has been noted, but this was not by any means always the case, and, as might be expected, any advantage accruing was of a more or less temporary nature, being removed by subsequent washing or dry-cleaning.

A moiré effect is obtained (all too often unintentionally) through the local pressure of one fabric on another. When the high points, such as the summits of ribs, in one fabric lie over similar high points in a contacting fabric and pressure is exerted, a glaze mark results which is of much greater intensity than the glazing in adjacent areas, where pressure is less. Suitable handling procedure enables the pattern obtained to be controlled within limits, and acetate rayon, being thermoplastic, is particularly suitable for such effects. If it is desired to combine with these moiré effects a silicone water-repellent finish, it should be noted that the moiré operation must be applied after padding and drying the silicone but before stoving, otherwise intensity of glazing contrast will be lost. It may be that this reduced glazing is associated with the smaller water absorption figure which results from silicone treatment, and it is interesting to note that this figure is less for fabric treated with silicones than with a number of other water-repellents. Table V shows the increase in weight of samples of acetate rayon fabric which have been treated with a variety of such agents, after immersion in water for 48 hr. and blotting off of surface moisture.

This may appear to be a somewhat crude test, but Table V shows that it is reasonably repeatable.

TABLE V

Water retained (%) by Variously Pretreated Acetate Rayon Fabric after Immersion for 48 hr. in Water and Surface Blotting

Pretreatment	Water retained (%)			
	Op. A*	Op. B*		Mean
Untreated	85	81	78	81
Soap–alum	62	62	64	63
Velan	77	75	73	75
Phobotex FT	82	77	74	78
Mystolene Filler (Catomance)	71	75	69	72
Beetle Resin BT 320 ...	64	63	57	61
Drisil 148	50	53	50	51

* Determinations have been made by two operatives, A and B, one determination being in duplicate.

(iii) SILICONES ON OTHER FABRICS

So far the effects of silicones have been considered on 100% acetate rayon taffetas. Table VI shows that satisfactory proofing with excellent fastness to dry-cleaning and reasonable wash fastness can be obtained on mixtures of acetate rayon with cellulose and even on cellulose alone.

Cellulose triacetate yarn, being fully acetylated, is even more hydrophobic in its own right than is the secondary acetate. In the natural state, Tricel, as the British Celanese product is called, absorbs only slightly over half the amount of water taken up by normal Celanese. In this respect, therefore, it approaches even more closely to the more expensive wholly synthetic fibres, Terylene, etc., and like them is laundered more easily and dried more quickly.

It is too early to have had much experience with water-repellent treatments on Tricel, but preliminary trials indicate that, as was to be expected, silicones can be applied in the same way as to secondary acetate, resulting in similar fastness properties.

(iv) OTHER SILICONE PROCESSES

So far, all silicone treatments described have utilised the ready-emulsified Drisil 148. As previously mentioned, this is a great convenience, but there are two points which should be weighed against this: it tends to produce more "marking" than does a well prepared Drisil 115 emulsion and it gives a somewhat stiffer handle. The latter point is not always a disadvantage and may in some cases be beneficial. But "marking" is never desirable, and its avoidance is worth some trouble. Where the stiffness imparted by Drisil 148 can be tolerated, such marking as cannot be avoided can usually be cured by a "knife" treatment in which the fabric is drawn, in open width, over a blunt knife edge, so giving an overall scraping or "marking" action.

Where a softer handle and minimum marking are desired, and where the fabric is of such construction that slipping is not likely to occur, the use of Drisil 115 is recommended. This is prepared by the somewhat complicated emulsifying procedure described above, using one of the recommended emulsifying agents. It is obvious from what has been said that only very efficient emulsifying agents can be used, but they must also have the property of evaporating or being destroyed during the curing operation. Otherwise water-repellency will be much impaired. The recommended agents are satisfactory in these details.

(v) COMBINED FINISHES

It may frequently be required that a fabric shall be both water-repellent and crease-resistant. Such combined properties are obviously most desirable in such materials as gaberdines and sometimes for suitings. A very considerably improved resistance to creasing results from the silicone treatment alone, and in a 100% acetate rayon fabric this cannot be improved by the use of urea–formaldehyde resins. Indeed, such resins have the reverse effect on acetate rayon, since penetration of the resin into the fibre is very slight, and the surface deposits which result give stiffness and brittleness. Normally, however, a blended fabric containing at least 50% viscose rayon is considerably improved in crease-resistance by the use of such crease-resist resins. They can be utilised on such blended fabrics admixed with silicone providing that the following precautions are observed. The silicone bath is prepared at double the normal working strength. CDMBAC is not suitable for this purpose, and either Drisil 115 with SE 100, or Drisil 148, should be used. The crease-resist solution also is made up at double working strength, and the two double-strength baths are mixed. When Drisil 115 with SE 100 is being used, it is necessary before mixing to adjust the pH of the crease-resist resin solution to 8·5, but no such adjustment is required when Drisil 148 is used. Our experience, however, is that little or no advantage is gained by such a combination in respect of crease-resistance but that fullness or stiffness is considerably increased.

TABLE VI

Water-repellency (Bundesmann) of Drisil 148 on Various Fabrics

Fabric	Finished		Washed						Dry-cleaned*					
No. of times	...	...	1		3		6		1		3		6	
	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)	(%)	(c.c.)
Acetate–viscose rayon blend	20	2	63·5	2	67·5	1	52·5	3·5	30·5	1	35	1	30·5	1
Acetate–viscose rayon gaberdine	24	5	43	6	70	1	72	1	19·5	4·5	20	5·5	50	2·5
Acetate–viscose rayon suiting ...	25	5·5	62·5	2·5	49	3	67·5	1	24·5	6	38	6	43	4
Cotton Nainbetter ...	22·5	1	47·5	2	64	3·5	76·5	6	31	2	30·5	1	42	3

* With tetrachloroethylene

Many modern fabrics are so constructed that the finisher has little margin to avoid "slipping" or "fraying". The silicones are very efficient lubricants and consequently in such a fabric may easily carry the slipping properties over the tolerance limit. In such cases it becomes necessary to incorporate an antislip material. One of the best of such agents is Syton 2X (Monsanto), and it is possible, by mixing the two separate baths, each at double working strength, to use this with Drisil 148 or with Drisil 115 prepared with SE 100 but not with CDMBAC. Such addition of Syton does not always adversely affect the handle.

Conclusion

An attempt has been made briefly to summarise the means at the disposal of the average finisher for giving a water-repellent finish to cellulose acetate fabrics and to assess the relative advantages of these methods for high-class work. Special attention has been given to the silicones on account of their superior properties, their comparative unfamiliarity, and the precautions needed in their handling, but it is emphasised once again that other, cheaper, and more easily handled materials can give good results when less severe conditions of use have to be met. Any would-be entrants into this field are cautioned against the too ready acceptance of apparently satisfactory laboratory results. It is definitely not safe to assume that a process is satisfactory until at least 2,000 yd. of fabric has been processed without fault.

* * *

I wish to thank the Directors of British Celanese Ltd. for permission to publish this paper, and my colleague Mr. G. F. Bull for the laborious and often disheartening work involved, particularly in the early stages.

BRITISH CELANESE LTD.
SPONDON
DERBY

(*MS. received 23rd February 1955*)

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PUBLICATIONS SPONSORED BY THE SOCIETY'S FASTNESS TESTS CO-ORDINATING COMMITTEE—XVI

An Investigation into some Methods for the Assessment of the Weathering Fastness of Dyed Textiles

E. BUTTERWORTH and J. C. GUTHRIE

Dyed textiles are, in general, less resistant to colour change when weathered than when exposed behind glass to daylight. No standard method exists for the assessment of weathering fastness. An outdoor weathering test and a wet fading lamp test are described, and their merits and deficiencies discussed. The method of assessment allows direct comparison between the weathering (or wet-fading-lamp) fastness of a pattern and the light fastness according to *B.S.* 1006. These methods have yielded useful results in practice, and this paper records some work carried out to date.

INTRODUCTION

The fastness of dyed materials to daylight is tested according to *B.S.* 1006 : 1955[1]. This test was designed for assessing the light fastness of dyeings which would be used mainly under cover or outdoors to daylight only and which would not be exposed to the weathering action to which certain fabrics, e.g. awnings, motor car hoods, pram hoods, are subjected. A dyeing will usually fade at a slower rate indoors than if fully exposed to the weather, and it cannot be assumed that the light fastness figure obtained according to *B.S.* 1006 is attained during complete exposure out of doors to sun, rain, frost, fog, and so on. It is therefore desirable to have a method of test for light fastness which takes account of weathering if the end-use of the dyeing is an outdoor one.

No instructions or recommendations for assessing the light fastness of dyeings in weathering tests exist in this country at present. In the U.S.A. it is claimed that the light fastness standards of the American Association of Textile Chemists and Colorists (AATCC) may be used unprotected in weathering tests, and the following is based upon their instructions[2]—

The standard dyeings (i.e. the AATCC light fastness standards)* will not bleed in rain water or mild scouring, and can therefore be used to test and grade the fastness of coloured textiles to weather. Testing may be done by actual outdoor

*The AATCC light fastness standards are blends of loose wool dyed with Eriochrome Azurole B and loose wool dyed with Indigosol or Algosol Blue AGG, in proportions varying from 100% of the former to 5% of the former plus 95% of the latter. Both dyes have good fastness to wet treatments.

exposure or in weathering lamps, any soil accumulated in the test being removable without effect on the colour. Outdoor exposures may be made exactly as defined for the Standard Sun Test, except that no glass covering is used; such exposures shall be carried out preferably in non-industrial areas. Weathering lamp tests may be made as described in the literature distributed by the manufacturers of the lamps.

Experiments which we have carried out suggest that the test methods referred to in the above paragraph are not entirely satisfactory. Also tests using unprotected *B.S.* 1006 standards exposed to the weather, or alternatively wet in a wet fading lamp, are of little value. Mention has been made in previous publications[3, 4] of results of tests to determine weathering resistance, and full details of the testing methods are described below. This is not intended to be a recommendation for a standard weathering test at this stage, but is a report on work carried out to date.

1. WEATHERING TEST

Exposures were carried out on the laboratory roof, where patterns were completely exposed to the weather. Fabric samples were held extended, at 45° to the horizontal facing south, by means of tapes attached to their corners. Yarn samples were fixed to cotton fabrics which were held as described above. *B.S.* 1006 standards were exposed under glass in the normal way for a daylight test. The completely exposed samples had to be taken down and washed before deciding whether fading had taken place or not. After the initial fade corresponding to Grade 4 on the Grey Scale[5], a piece of the faded fabric was cut off, and the remainder left for further exposure. It was found more convenient to follow the fades on the standards, since daily examinations of the exposed patterns required extensive washing. The actual assessment was carried out when the weathered patterns showed changes equivalent to 4 and 3 on the Grey Scale. Initially each of the eight *B.S.* 1006 standards was also completely exposed, but standards 1–6 were not fast to the washing which was necessary to clean them. *B.S.* 1006 standards are therefore not suitable for tests involving their complete exposure to the weather. The AATCC claims that its standards may be used for weathering tests in which they undergo the same exposure conditions as the patterns[6]. By simultaneously exposing samples of the patterns under glass alongside the *B.S.* 1006 standards a direct comparison between daylight and weathering fastnesses may be obtained.

The results of these tests showed that, compared with the samples under glass, the completely exposed samples were usually rated lower on the light fastness scale. Table I contains results which have appeared earlier[3], and quotes the fastness of weathered patterns in terms of *B.S.* 1006 standards exposed under glass.

Since this procedure involves the fading of standard patterns according to *B.S.* 1006, the assessments clearly indicate the difference in the fastness of the samples to indoor and outdoor exposures, which varies in the above table from ½ to 3 points. Thus if Indian yellow is used continuously out of doors its "light fastness" will in effect be reduced from 6 to 4. On the other hand, criticism of the test is legitimate on the grounds that standards and weathered patterns have not been exposed under exactly the same conditions. If this was insisted upon for a weathering test, then it would be necessary to establish a set of weathering standards. This would take a considerable time, and as a temporary measure it is submitted that the procedure described above is simple and gives useful results, particularly in the direct comparison between normal fading and weathering, and also in detecting patterns which have poor resistance to weathering.

TABLE I

Pattern	Weathering Fastness	Light Fastness (*B.S.* 1006)
Sulphur	3–4	6
Indian yellow	4	6
Pink	4	5–6
Red	4	6–7
Light blue	4–5	5–6
Medium blue	5	6–7
Dark blue	5	6–7
Apple green	4	5–6
Malachite green	5	6–7
Black	5	8
Brown	5	7
Khaki	5	7
Tan	5	7
Maroon	3	3–4

In order to obtain information on the effect of time of the year on the results of weathering tests, sets of AATCC standards and a range of pigmented yarns were completely exposed to the weather, similar sets being started at intervals of one month. In each case *B.S.* 1006 and AATCC standards were also exposed under glass in the normal way.

The AATCC standards are more in line after exposure to the weather, chiefly because the same two dyes are used for each standard, but they fade much more rapidly than when under glass and also are dulled after exposure. Typical results are shown in Table II, where the assessments of the weathered AATCC standards are made in terms of AATCC standards exposed under glass.

The assessments are reasonably constant for the different initial exposure times, but the assessments of the weathered standards are not in strict geometrical progression. The highest assessment of standard 8 exposed to the weather is 5–6, which is a reduction of 2½ points, and the scale for exposed patterns is reduced considerably compared with the daylight ratings.

Exposures of a series of spun-dyed Fibro yarns were staggered by periods of 1 month in their initial exposure times. Assessments in terms of *B.S.* 1006 standards faded under glass in the normal way were extremely variable, and many assessments were higher than the assessment

TABLE II

Assessment of Weathered AATCC Standards in terms of AATCC Standards faded under Glass

Standard No.	8 Oct. 1953	27 Oct. 1953	1 Dec. 1953	14 Jan. 1954	17 Feb. 1954	4 March 1954
2	2	2	2	2	2	2
3	2	2	2	2	2	2
4	2–3	2–3	2–3	2–3	2–3	2–3
5	3–4	3–4	3–4	3	4	4–5
6	4	4	4	4	4–5	5
7	5	4–5	4–5	5	5	5
8	5–6	5	5	5–6	5–6	5–6

by the normal daylight test. The samples were washed only at infrequent intervals, and it was assumed that dirt on the patterns had shielded them and inhibited fading. In support of this was the fact that two series of samples showed greater degrees of fade than others which had been put out for exposure two to three months earlier. This effect of a coating of dirt is an unpredictable factor, which is a definite disadvantage of outdoor weathering tests in industrial atmospheres.

Since weathering causes accelerated fading compared with fading according to *B.S.* 1006, the duration of weathering tests will be less than that of daylight tests, but even so, fairly long times may be involved. Accordingly, we have used a wet fading lamp test, which is quicker and also does not suffer from the soiling effects of outdoor weathering.

2. WET FADING LAMP TESTS

(*a*) *Samples sprayed throughout Exposure*

Several accounts have been given of weathering lamps[6–8], which are used chiefly in the paint industry, and Marney[9] has described a method of modifying a fading lamp so that the patterns may be sprayed with water periodically throughout the exposure. In Marney's method the *B.S.* 1006 standards are sprayed alongside the patterns. In a recent modification to Marney's method the standards are kept dry in a Perspex (ICI) box whilst water is sprayed, and assessments of the weathering fastness of some vat and azoic dyes have been quoted[10].

Since we have found that *B.S.* 1006 standards bleed, we have modified a fading lamp on similar lines to those of Marney, except that the standards are not sprayed with water. The water annulus normally fitted to this fading lamp is removed, and two lugs *A* and *B* (Fig. 1) on the carriage, rotating anticlockwise, alternately switch a water spray off and on. This simple modification can be applied to any existing type of fading lamp provided that the samples are on a carriage which rotates around the light source.

By placing standards and patterns behind lug *A*, these will fade as in the ordinary fading lamp, whilst patterns following *B* will be kept wet throughout the exposure. The carriage rotates at about 1 r.p.m., so that wet patterns never get dry. Their temperatures oscillate between 77° and 90°F., being at the lower temperature immediately after spraying. Fig. 2 shows two curves of moisture regain of patterns against time in the fading lamp. One refers to patterns kept dry when the instrument is used as a wet fading lamp, and the other is the curve for patterns with the lamp used for normal fading with the water annulus removed. The curves are close together, and it is permissible to say that, over 22-hr. exposure periods, fading of the dry standards takes place under the same moisture conditions as occur in the normal test in this fading lamp.

It is therefore possible to assess patterns in this modified fading lamp for both dry and wet conditions, and so obtain a direct comparison. Wet fading lamp assessments quoted elsewhere[3, 4] were

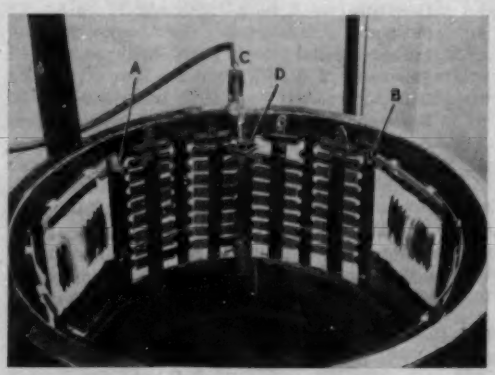

FIG. 1—Wet Fading Lamp

A and *B* are lugs which engage with *D*. *D* is attached to the water spray tube with water inlet *C*. Every revolution of the sample carriage causes the lug *B* to switch on the spray and *A* to switch it off. The standards are shown between *A* and *B*. The patterns consist of yarns mounted on cotton fabrics.

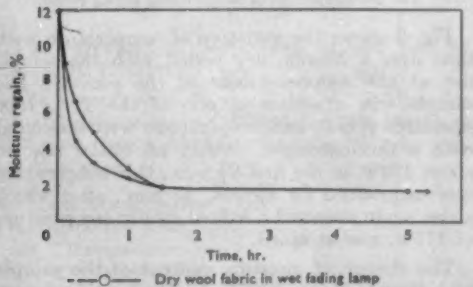

FIG. 2

obtained by this method. Table III lists assessments, in terms of the dry AATCC standards, of AATCC standards kept wet in a fading lamp.

TABLE III

Assessment of Wet AATCC Standards in terms of Dry AATCC Standards

Standard	Assessment
2	2
3	2
4	2
5	2
6	3
7	4
8	5

Comparison with Table II shows that the wet fading lamp has been more severe on the AATCC standards than the weathering exposures. Hence, if the AATCC standards are used as wet standards in a wet fading lamp, patterns would probably be rated higher than if assessed against completely exposed AATCC standards in a weathering test.

(*b*) *Samples subjected to Alternate Wet and Dry Cycles during Exposure*

Another possibility with the wet fading lamp is a cycle of wetting the patterns, followed by no spraying, and then spraying again, etc. The time cycle is arbitrary and the possible number of variations is enormous, but we have carried out some exposures in which the samples were kept wet for 30 min., allowed to dry for 30 min. during exposure, and so on.

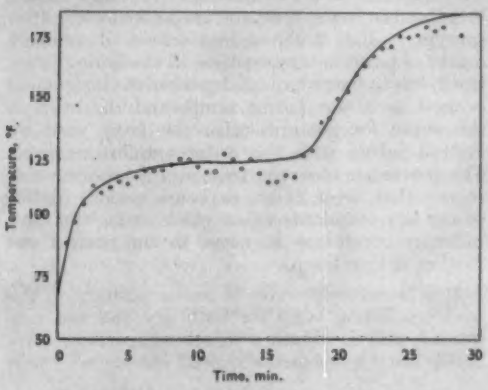

FIG. 3—Temperature of Sample during Drying Period

Fig. 3 shows the variation of temperature with time over a 30-min. dry period with the sample wet at the commencement of the period. The sample was a square of one of the *B.S.* 1006 standards (wool), and temperatures were measured with a thermocouple. After an initial rise to about 120°F. in the first 2½ min., this temperature was maintained for approx. 13 min., after which a rise again occurred. A final steady temperature of 175°F. was attained.

The change of moisture content of the sample with time is shown in Fig. 4. During this drying period a variety of conditions occur, and the fading could depend on the actual cycle times decided upon. For example, if 1-hr. cycles were used, the samples would be fading for the last half-hour of the dry period at the same rate as in a standard fading lamp test. For times of 15 min. or less these conditions would never be reached.

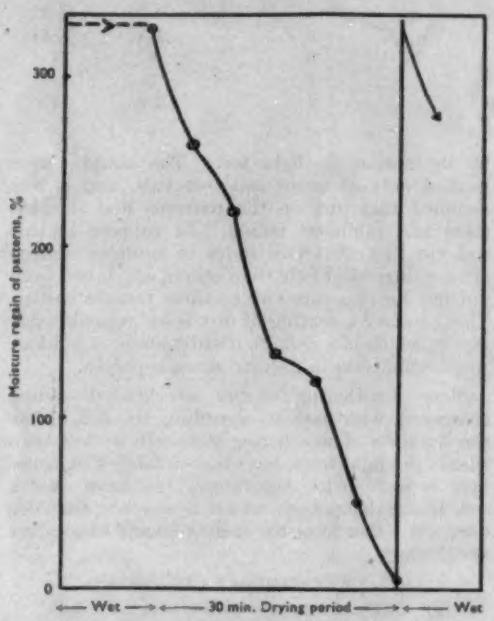

FIG. 4—Variation of Moisture Regain of Samples of Wool Fabric with Time during a 30-min. Drying Period

TABLE IV

Wet Fading Lamp Assessments

Pattern	Patterns exposed to 30-min. Wet and Dry Periods	Patterns wet continuously
Maroon	3–4	3–4
Light blue	4	3–4
Medium blue	4–5	4
Dark blue	6	4–5
Sulphur	5–6	5
Indian yellow	5	5
Pink ...	5	5
Red ...	6	6
Brown ...	6	6
Apple green	6	5

The results of fading some samples by both the above methods in the wet fading lamp are given in Table IV. Of the ten samples, five were assessed lower in the all-wet test, and five equal in each test. The all-wet test is therefore possibly more severe than the 30-min. wet and dry cycling.

(*c*) *Comparison of Results from Weathering and Wet Fading Lamp Tests*

Fig. 5 shows assessments after weathering plotted against assessments after exposure in the wet fading lamp with continuous spraying, for a number of samples. The number of plots is not large, but they are distributed on both sides

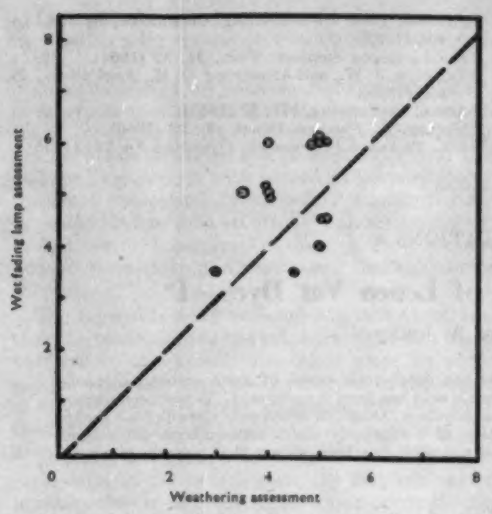

FIG. 5

of the line which represents the same assessment by each test. There is a bias towards higher values in the wet fading lamp, but further work is desirable before any conclusions can be drawn.

DISCUSSION

The results which have been obtained to date [3, 4] have shown that these tests can be used to predict resistance to loss of colour of textiles during outdoor exposure. The lamp test has proved the more convenient, and it satisfactorily selects patterns which should not be used out of doors. Outdoor exposure at Droylsden has certain limitations, chiefly because of the dirty atmosphere. We have several times observed patterns which had become really dirty, and the dirt had protected the pattern. It is therefore necessary to keep the sample clean, which entails frequent washings.

The British Standards *B.S.* 1006, with the exception of possibly 7 and 8, are unsuitable for outdoor exposures. The AATCC standards can be used exposed out of doors, but the scale is then effectively reduced from 8 to 5–6. Many samples have been tested which are better than the upper end of the range of wet AATCC standards, and an extended scale is desirable. The provision of a special set of weathering standards for these tests is desirable, but is likely to be a lengthy undertaking, in view of the work which has been involved in establishing the *B.S.* 1006 standards. Until such weathering standards are established, it is necessary to be able to test patterns, and the tests described are considered to give reliable information.

The objections to these methods are based mainly on the fact that the patterns and the standards do not experience the same treatment. Also, it is possible to criticise the procedure of keeping the patterns in the wet fading lamp soaking wet throughout, whereas a series of successive wet and dry cycles might be preferable. The first objection would require the establishment of new standards, and the second may be answered by the fact that so far we have found continuous wetting to be at least as severe as wet and dry cycling. Reproducibility in the wet fading lamp is good.

The advantage of the above methods is that a direct comparison is obtained between the behaviour of patterns allowed to fade (1) normally by daylight and (2) by weathering or fading lamp.

Our experience to date has shown that samples assessed at 5 or higher in the wet fading lamp test are of suitable fastness for outdoor use.

Owing to possible inconsistencies in the weathering test which have not yet been resolved, it has been decided that the wet fading lamp test is to be preferred for assessing patterns for resistance to outdoor exposure. It is not claimed that this test is an ideal one, but its practical value is well established in these laboratories in that it successfully eliminates samples which are not likely to withstand weathering.

CONCLUSIONS

1. As a general rule samples are less resistant to colour change when weathered than when exposed to daylight behind glass.

2. *B.S.* 1006 standards are unsuitable for use completely exposed in weathering or wet fading lamp tests.

3. AATCC standards are less fast when completely exposed in weathering or wet fading lamp tests; many patterns are superior to them in fastness, and the scale is not sufficiently extensive at the upper end.

4. The methods described, where the standards are faded normally and the patterns either weathered or kept wet in the fading lamp, give a measure of the resistance to weathering which can be compared directly with the normal daylight assessment. The wet fading lamp test is preferred at present owing to the unpredictable effects of soiling on the assessment of outdoor weathering exposures.

5. The setting-up of a scale of new weathering standards will be a long-term process. These methods have given useful results in practice, and are considered the best available until suitable weathering standards are established.

* * *

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RESEARCH LABORATORIES
COURTAULDS LTD.
DROYLSDEN
MANCHESTER

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COMMUNICATIONS

The Chemistry of Esters of Leuco Vat Dyes—I*

S. AINSWORTH and A. JOHNSON

The oxidation, with acidic hydrogen peroxide, of the disulphuric esters of leuco anthraquinone-2-sulphonic acid and of leuco indigo-5:7:5':7'-tetrasulphonic acid has been investigated. It has been shown that direct oxidation of the ester occurs and is mainly a univalent change, in which only one sulphate group is eliminated from the ester, leading to the formation of a relatively stable semiquinone derivative. Oxidation with nitrous acid has been examined briefly, and it has been shown that oxygen plays an important part.

Introduction

The disulphuric ester of leuco indigo was first prepared in 1879 by A. von Baeyer [1] using alkaline potassium pyrosulphate as the esterifying agent. He was unable to isolate the ester, but demonstrated that indigo could be precipitated from its solution by the action of acidic ferric chloride. However, the importance of these reactions for the application of vat dyes was not realised until some forty years later. In 1921 the disulphuric esters of leuco indigo and some of its derivatives were first isolated in good yield by Bader and Sunder [2], who are now regarded as the discoverers. The disulphuric esters of leuco vat dyes have since come to be widely used for producing pale, level dyeings and, more particularly, for textile printing.

In Bader's preparation the leuco vat dye was isolated and then esterified, by the method due to Verley [3], with chlorosulphonic acid in anhydrous pyridine. The resulting pyridinium salt of the sulphuric ester was then decomposed by treatment with alkali (I: D = vat dye nucleus).

Although other methods, which make it unnecessary to isolate the free leuco compound, have since been introduced [4], the essential chemical changes of reduction followed by esterification are clearly demonstrated in Bader's synthesis—

$$O{=}D{=}O \xrightarrow{\text{Reduce}} HO\text{–}D\text{–}OH \xrightarrow[2C_5H_5N]{2HSO_3Cl} [O_3S\text{–}O\text{–}D\text{–}O\text{–}SO_3]^{2-},2C_5H_5N^{+} \xrightarrow{2NaOH} NaO_3S\text{–}O\text{–}D\text{–}O\text{–}SO_3Na + 2C_5H_5N + 2H_2O \quad \text{(I)}$$

By whatever method the leuco vat dye is applied, the insoluble vat dye is regenerated on the fibre by treatment with an oxidising agent (nitrous acid, dichromates, or, in printing, chlorates in the presence of a catalyst) under acidic conditions.

It has been generally concluded that development occurs by a formal reversal of Bader's method of synthesis, i.e. by hydrolysis of the ester to the leuco compound followed by oxidation of this to the vat dye—

$$NaO_3S\text{–}O\text{–}D\text{–}O\text{–}SO_3Na + 2H_2O \rightleftharpoons HO\text{–}D\text{–}OH + 2NaHSO_4$$

$$HO\text{–}D\text{–}OH \xrightarrow{O} O{=}D{=}O + H_2O \quad \text{(II)}$$

However, no experimental confirmation of this mechanism has been offered, and little consideration paid to its implications. Bader came later to the opinion that development did not occur by this route [5] and favoured the hypothesis that the ester groups are eliminated by direct oxidation rather than by hydrolysis. He stated that it is a characteristic property of the $-SO_3Na$ group to be more labile when it is joined to oxygen or nitrogen than to carbon [6]. Although the universal validity of the principle may be questioned, it is certainly applicable to the sulphuric esters of leuco vat dyes (and also to diazosulphonates) under acidic oxidising conditions.

Mechanism II can be shown to be inappropriate by the following argument, in which the effect of different relative velocities of hydrolysis and esterification (1 and 2 in II) on the results of non-oxidative acidification is considered—

(i) If hydrolysis is relatively rapid, the position of equilibrium will be to the right, and a considerable proportion of ester should be converted to the leuco compound.

(ii) If hydrolysis and esterification occur at approximately the same rate, the yield of leuco compound will be less than in (i).

(iii) If esterification is relatively rapid, the result will be the opposite of (i) and, in the limiting case, hydrolysis will not occur and no leuco compound will be formed.

* Based in part on a lecture given by A. Johnson to the Manchester Section at the Textile Institute, Manchester, on 18th December 1953, Mr. F. Farrington in the chair.

These equilibrium states should also be reached by treating a leuco compound with dilute sulphuric acid.

Observations of the behaviour of the leuco esters in practical applications do not, however, bear out these conclusions. In the presence of reducing agents, acidic solutions can be kept at or near the boil for long periods with no obvious separation of the leuco compound. Free leuco compounds may be suspended in acid solutions without formation of the ester. Esterification does, in fact, require powerful esterifying agents used in anhydrous solvents.

The general body of evidence suggests, therefore, that the conversion of the sulphuric ester of a leuco vat dye to the parent dye takes place by some mechanism other than the hydrolysis of the whole of the ester to the leuco compound followed by a distinct oxidation of this to the vat dye.

The work which is described in this paper represents, so far as is known, the first systematic investigation of the reactions which occur during development.

For the remainder of this paper the term *vat ester* will be used as a generic name for the disulphuric esters of leuco vat dyes.

Experimental and Results

1. WITH COMMERCIAL DYES

Materials

INDIGOSOL O4B (DH)—Two specimens were used. Sample 1 was available from some earlier work. It had been supplied with a low electrolyte content by the manufacturers, and subsequently had been stored in a refrigerator. The ester content was shown by analysis to be 50%. Sample 2 was supplied by the manufacturers and had an ester content of 96%.

CIBANTINE BROWN G (Ciba)—A purified sample was available.

SOLEDON JADE GREEN (ICI)—A commercial sample containing 33% of the ester.

SOLEDON BLUE 4BC (ICI)—A sample supplied by the manufacturers and containing only added sodium carbonate. It was purified by repeated extraction with acetone followed by precipitation with chloroform.

These samples of commercial dyes of varying degrees of purity were used only for exploratory experiments, specially prepared compounds being used for the later work.

Hydrolysis

A solution of Indigosol O4B (Sample 1) was placed in a flask fitted with a bent side-arm connected by a ground glass joint. Dilute hydrochloric acid was placed in the side-arm. The whole apparatus was evacuated and closed, and the solutions were mixed by rotating the side-arm about the ground joint. Any reaction, therefore, took place under non-oxidising conditions. The concentrations after mixing were—vat ester 10 g./litre and hydrochloric acid 1 N. No visible change occurred in 24 hr.

When the experiment was repeated with the addition of 10 g. of sodium nitrite per litre, tetrabromoindigo was precipitated within 2 min.

Similar observations were made with Soledon Jade Green.

These experiments indicate that complete hydrolysis of the vat ester to the leuco compound does not occur during the time required for normal development.

Oxidation

No reaction occurred between Indigosol O4B and alkaline hydrogen peroxide. With acidic hydrogen peroxide the vat dye was slowly precipitated, the reaction solution first becoming green. Addition of ferrous sulphate to the acidic solution brought about a marked increase in the rate of formation of the vat dye. Similarly, the vat ester was oxidised slowly with acidic ammonium persulphate. The rate was increased by addition of ferrous iron.

Since the system Fe^{++}–H_2O_2 is known to produce both hydroxyl (OH) and perhydroxyl (OOH) radicals[7, 8], it is reasonable to assume that these radicals are responsible for the increase in rate caused by the addition of ferrous sulphate.

Further experiments in an evacuated apparatus were performed with all four vat ester samples, using hydrogen peroxide with ferrous sulphate and also nitrous acid as oxidising agents. The proportions of vat ester to oxidising agent were varied, but the vat ester was always present in excess. The reactions were allowed to continue until precipitation of the vat dye appeared to be complete. The precipitate was then collected and weighed, but it was not always possible to effect a complete separation at the filter, particularly when much vat ester remained unchanged. Any remaining vat ester in the filtrates was oxidised to the vat dye by addition of sufficient sodium nitrite, so that it was possible to estimate roughly the extent of the original oxidation.

Although these experiments did not yield accurate results, a general feature was that the apparent yield of vat dye was often greater than that expected from the proportion of oxidising agent taken. Also, the colours of the vat dye precipitates were duller than the colours of authentic samples. However, the precipitates could all be reduced with alkaline hydrosulphite, yielding solutions in which cotton could be dyed normally. The significance of these observations will be discussed later.

2. WITH NUCLEAR-SULPHONATED ESTERS

Normal vat esters, which yield the insoluble vat dyes on oxidation, are not very convenient for measurements of rate of reaction, since the reaction mixture does not remain homogeneous. Nevertheless, it was thought that measurements of rates of reaction under a variety of conditions and for as many components of the system as possible would be of value.

Experiments were performed with the vat esters derived from (*a*) indigo-5:7:5′:7′-tetrasulphonic acid and (*b*) anthraquinone-2-sulphonic acid. Thus,

the expected end-products of oxidation were indigo-5:7:5′:7′-tetrasulphonic acid and anthraquinone-2-sulphonic acid respectively, both of which are soluble in water. The reaction mixture would, therefore, remain homogeneous, thus facilitating the removal of truly representative portions for analysis.

Materials and Preparations

(i) INDIGO-5:7:5′:7′-TETRASULPHONIC ACID—This was prepared by the direct sulphonation of indigo (Bloxam[9]). The tetrasodium salt was obtained by treating the diluted reaction solution with excess of sodium acetate. It was purified by extraction with ethanol and recrystallised from aqueous ethanol.

(ii) VAT ESTER OF INDIGO-5:7:5′:7′-TETRASULPHONIC ACID—This was prepared by a modification of the commercial manufacturing method*. Pyridine sulphuric anhydride was prepared by adding chlorosulphonic acid (19 g.) dropwise, with stirring, to dry pyridine (50 ml.) at 0°C. An intimate mixture of the sodium salt of indigotetrasulphonic acid (14 g.) and copper powder (4 g.) was then added slowly, and the mixture heated at 70–75°C. for 2 hr., cooled, and poured into 300 ml. of sodium carbonate solution (50 g./litre). After 12 hr. sodium hydroxide (10 g.) was added, the mixture heated at 40°C. for 15 min., the brown copper residue removed, and the volume reduced to 150 ml. by vacuum evaporation. The indigosol was precipitated by adding ethanol (150 ml.). It was freed from much inorganic matter by fractionally precipitating from water with ethanol, and finally purified by chromatography on an alumina column. The chromatogram was developed with 50% aqueous ethanol, the vat ester moving in a colourless band which fluoresced blue in ultraviolet radiation. It was finally obtained as a white powder, which dissolved readily in water to give a clear solution with a bright blue fluorescence. It was stored in a vacuum over silica gel. (Found: C 20, H 1·2, S 20, N 2·4%; $C_{16}H_6S_6N_2O_{20}Na_6$ requires C 22, H 0·7, S 22, N 3·2%)†. When the vat ester was oxidised with excess of nitrous acid, the calculated yield of indigotetrasulphonic acid was obtained, as measured colorimetrically (see next section).

(iii) ANTHRAQUINONE-2-SULPHONIC ACID—The barium salt was precipitated by addition of barium chloride to a solution of the sodium salt of anthraquinone-2-sulphonic acid. It was collected and boiled with 10% sulphuric acid, the precipitate of barium sulphate removed, and the solution concentrated. Crystalline anthraquinone-2-sulphonic acid separated on cooling and was collected, washed with concentrated hydrochloric acid, and dried over phosphorus pentoxide and potassium hydroxide in a vacuum (Fierz-David[10]). The sodium salt was obtained by adding sodium hydroxide solution to a hot aqueous solution of the free acid until a persistent turbidity was produced. It was obtained as small glistening plates on cooling.

* D. A. Fairweather and ICI, private communication.

† Microanalyses by Drs. Weiler and Strauss, Oxford.

(iv) VAT ESTER of ANTHRAQUINONE-2-SULPHONIC ACID—This was prepared from the sodium salt of the sulphonic acid by the method given above under (ii). It was purified by extraction with methanol followed by repeated precipitation from solution in methanol by adding ether, being finally obtained as a light yellow powder. It dissolved readily in water to give a clear solution with a blue fluorescence. It was stored over silica gel in a vacuum. On oxidation with excess of nitrous acid the calculated yield of anthraquinone-2-sulphonic acid was obtained (for colorimetric analysis, see next section).

(v) All other materials were of AnalaR quality.

Analysis of Reaction Solutions

Aliquot portions of reaction solutions were removed from time to time for analysis. Concentrations of the different components were determined colorimetrically (see below) with a Spekker photoelectric absorptiometer (Hilger & Watts) with a mercury-vapour discharge lamp as illuminant and appropriate filters.

(*a*) INDIGO-5:7:5′:7′-TETRASULPHONIC ACID AND THE CORRESPONDING VAT ESTER—These could be determined directly in light of wavelength 3650 A. for the vat ester and of wavelength 5770–5790 A. for the sulphonic acid. The optical density measured at 3650 A. when both compounds are present in the same solution includes a contribution from indigotetrasulphonic acid, which also absorbs light of this wavelength. However, this could be allowed for by subtracting a value corresponding to the known concentration of indigotetrasulphonic acid, as obtained from the optical density measured at 5770–5790 A. Since any intermediate compounds formed during a reaction may interfere to an unknown extent in the determinations, the values so obtained are referred to as concentrations of "analytical indigo" and "analytical indigosol"[11].

(*b*) ANTHRAQUINONE-2-SULPHONIC ACID AND THE CORRESPONDING VAT ESTER—Since both these compounds have similar absorptions at all wavelengths available with the absorptiometer, direct determination of their separate concentrations when in admixture was not possible. The quinone was determined by diluting an aliquot portion of the reaction mixture with an equal volume of N. sodium hydroxide solution containing sodium hydrosulphite (100 g./litre) and measuring the optical density of the resulting red solution of the quinol at 4360 A. The absorption of the vat ester at this wavelength is insignificant. For the reason already given, the concentrations so obtained are expressed as "analytical quinone".

(*c*) NITROUS ACID—A 5-ml. portion of the reaction solution was added to 5 ml. of a solution containing sulphanilic acid (1 g.) in 30% acetic acid (100 ml.). A solution (5 ml.) containing *α*-naphthylamine (1 g.) in 30% acetic acid (100 ml.) was immediately added, and the volume made up to 25 ml. with water. After standing for 5 min., the optical density of the solution of 4-*p*-sulphophenylazo-1-naphthylamine was measured at

wavelength 5000–5400 A. A correction was applied for the absorption of indigotetrasulphonic acid in this region.

(*d*) HYDROGEN PEROXIDE—This was determined by the colorimetric method of Ovenston and Rees[12]. An aliquot portion of reaction solution was added to a solution containing potassium iodide and ammonium molybdate. After standing for 5 min. in the dark and dilution to an extent appropriate to the original concentration of hydrogen peroxide, the optical density of the iodine solution was measured at wavelength 3650 A. The optical density should not exceed 1·5, and the concentrations of potassium iodide and ammonium molybdate in the final solution should be 0·1 M. and 0·05 g./litre respectively. The absorption of vat ester at this wavelength was allowed for by placing a suitably diluted reaction solution in the comparison cell.

(*e*) SULPHATE IONS—Because the vat ester concentrations were low and small volumes only could be taken for analysis, the normal gravimetric method for the determination of sulphate could not be used. The following colorimetric method was devised and found satisfactory—A 5-ml. portion of reaction solution (max. concn. of sulphate = 0·001 M.) was added to 5 ml. of a 0·001 M. solution of barium chloride in 50% ethanol containing 5 ml. of Methyl Red solution (0·5 g./litre) per 100 ml. After allowing to stand for 5 min. to allow precipitation of barium sulphate, dilute ammonia was added to the Methyl Red end-point, followed by 5 ml. of 0·0015 M. potassium chromate solution. The volume was made up to 20 ml. with water, and the mixture allowed to stand for 5 min. to complete precipitation of barium chromate, which is insoluble in neutral and alkaline solutions. The solution was then filtered, giving a filtrate which contained chromate ions equivalent to the original sulphate and the concentration of which could be determined colorimetrically at wavelength 3650 A. The absorption of vat ester at this wavelength was allowed for as before. This method is a variation of the titrimetric method of Foster[13], but differs in the important respect that potassium chromate is used under neutral conditions only, thereby avoiding oxidation of the vat ester during the determination.

Measurement of Rates of Reaction

1. REACTIONS UNDER NITROGEN

Apparatus and Method

The experiments were performed in the apparatus shown in Fig. 1. Vat ester solution, containing either hydrogen peroxide or sodium nitrite, was placed in limb *A* and hydrochloric acid in limb *B*. The vessel *C* was placed in position, and Wembley nitrogen (oxygen content below 10 p.p.m.) passed through taps T_1 and T_2 for 30 min. During this time the apparatus was clamped in a thermostat bath. A few minutes before mixing, water from the thermostat was circulated through the jacket of *C*.

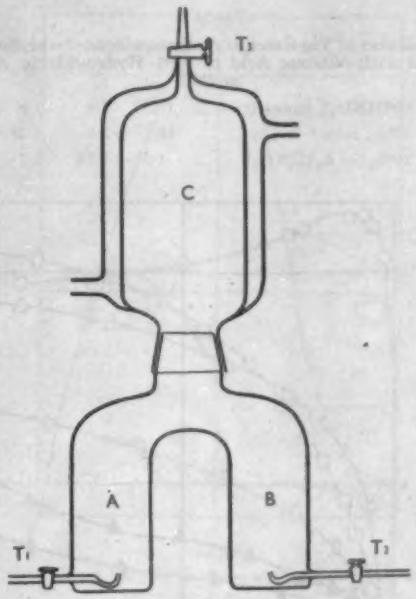


FIG. 1

To start the reaction, all three taps were closed and the apparatus was shaken gently. It was then clamped in the inverted position. Aliquot portions for analysis were withdrawn from time to time through T_2. All experiments were performed at 25°C. in the dark.

(*a*) *Reactions with Nitrous Acid*

A selection of the results is given graphically in Fig. 2 and 3, which show the effect of varying conditions on the rate of formation of analytical indigo and analytical quinone respectively. The rate of consumption of nitrous acid is also shown. To avoid confusion, the rate of disappearance of analytical vat ester is not shown, but the curves lie above the corresponding curves for analytical indigo. This demonstrates the presence of intermediate compounds.

Increasing the concentration of either nitrous acid or hydrochloric acid increases the rate of oxidation. However, the effect of hydrochloric acid is greater than that of nitrous acid.

The curves showing the consumption of nitrous acid have a pronounced irregularity at an early stage, in which nitrous acid is apparently being re-formed. The same effect was observed in the spontaneous decomposition of nitrous acid under similar conditions. These effects were shown to be caused by traces of oxygen left in the apparatus. Fig. 4 illustrates the effect of oxygen on the consumption of nitrous acid and the formation of analytical indigo. In the presence of air the rate of formation of analytical indigo is increased, whilst the apparent consumption of nitrous acid is decreased. Also, the irregularity on the nitrous acid curve is more pronounced.

TABLE I

Oxidation of Vat Ester of Anthraquinone-2-sulphonic Acid with Nitrous Acid in 0·1N. Hydrochloric Acid at 25°C.

$10^3[HNO_2]$, moles/litre ...	10	1·4	1·0
10^3k_1, min.$^{-1}$	18	2·5	1·7
10^3k_2 ($= k_1/[HNO_2]$) ...	1·8	1·78	1·7

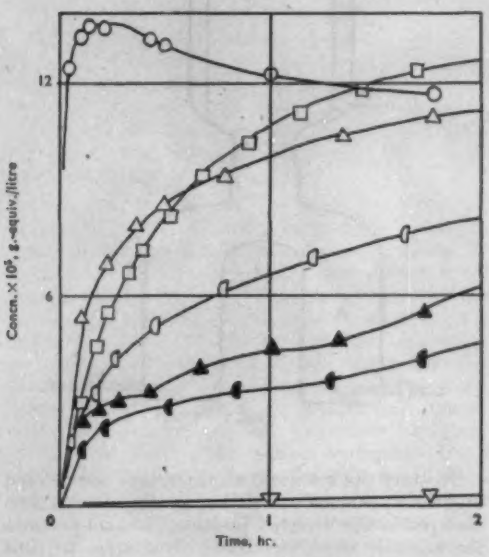


FIG. 2—Oxidation of the Vat Ester of Indigotetrasulphonic Acid ($6{\cdot}5 \times 10^{-5}$M.) with Nitrous Acid at 25°C.

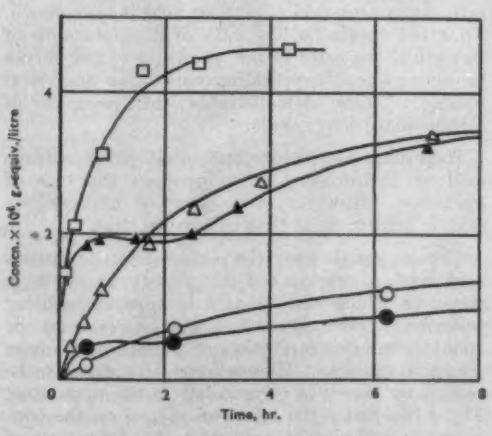


FIG. 3—Oxidation of the Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4}M.) with Nitrous Acid in 0·1N. Hydrochloric Acid at 25°C.

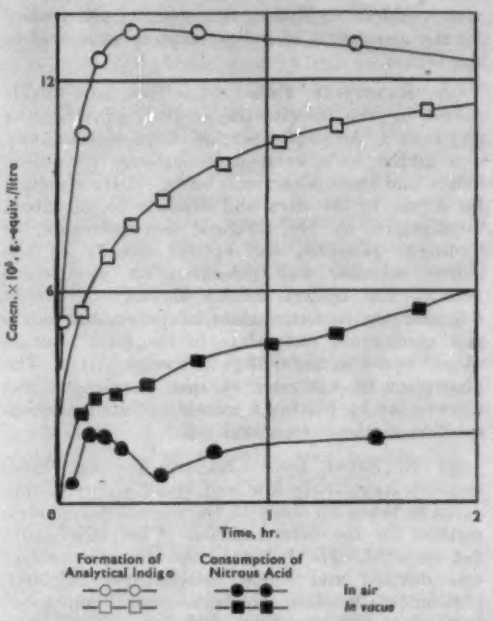


FIG. 4—Effect of Air on the Oxidation of the Vat Ester of Indigotetrasulphonic Acid ($6{\cdot}5 \times 10^{-5}$M.) with Nitrous Acid ($1{\cdot}3 \times 10^{-4}$M.) in 0·5N. Hydrochloric Acid at 25°C.

Plots of log $(a - x)$ against time (where a = initial concentration of vat ester and x = concentration of analytical indigo or of analytical quinone at time t) are linear for a considerable part of the reaction, particularly following the irregularity on the nitrous acid curves. This part of the reaction is, therefore, of the first order with respect to the vat ester. Moreover, for the anthraquinone derivative, the first-order rate constants are proportional to the initial concentration of nitrous acid (Table I). Thus, the rate-controlling reaction in this region is bimolecular between vat ester and nitrous acid (or an entity produced rapidly from nitrous acid in the stoichiometric ratio of 1 : 1).

(*b*) *Reactions with Hydrogen Peroxide*

Fig. 5 shows the effect of increasing the initial concentration of hydrogen peroxide on the oxidation of the vat ester of indigotetrasulphonic acid. The rate of change of concentration of hydrogen peroxide is also given. Fig. 6 represents the oxidation of the vat ester of anthraquinone-2-sulphonic acid and also shows the effect of including ferrous iron.

Initially the concentration of hydrogen peroxide appears to rise above that originally taken, even though vat ester is being decomposed at the same time. It was shown that this rise was caused by traces of oxygen remaining in the apparatus. Fig. 7 shows the results of measuring the apparent hydrogen peroxide concentration of acidified solutions of the anthraquinone derivative to which hydrogen peroxide had not been added. The solutions in one experiment had been swept with

nitrogen as already described. The other two experiments were performed with solutions made with ordinary distilled water, without any other treatment, on two different days. The figure illustrates the formation and the decay of a species capable of oxidising iodide ions to iodine under the analytical conditions. Since molecular oxygen does not oxidise potassium iodide under these conditions, the oxidant must have been produced by a reaction of oxygen with the vat ester and acid.

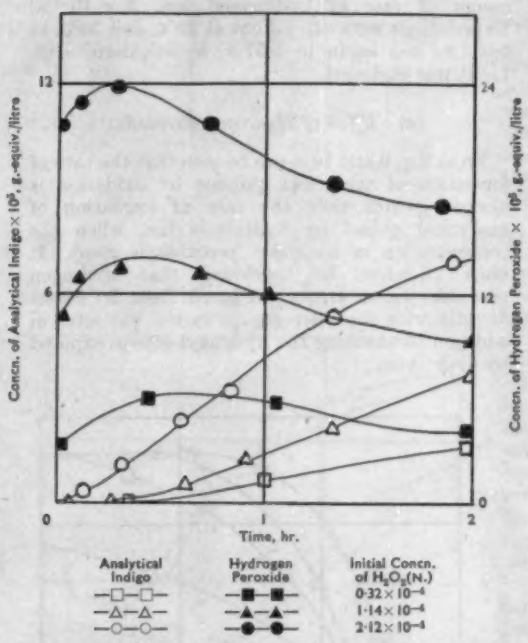


FIG. 5—Oxidation of the Vat Ester of Indigotetrasulphonic Acid ($6{\cdot}5 \times 10^{-5}$M.) with Hydrogen Peroxide in 0·5N. Hydrochloric Acid at 25°C.

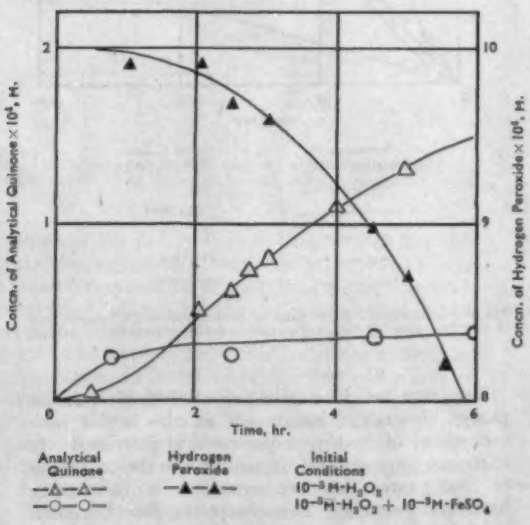


FIG. 6—Oxidation of the Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4}M.) with Hydrogen Peroxide in 0·1N. Hydrochloric Acid at 25°C.

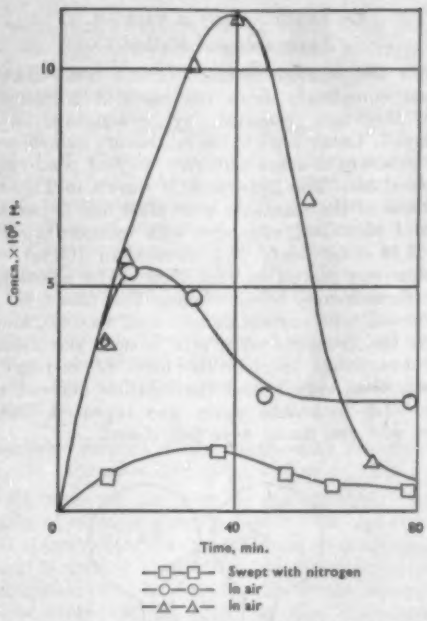


FIG. 7—Apparent Formation of Hydrogen Peroxide in Solutions of the Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4}M.) in 0·1N. Hydrochloric Acid at 25°C.

The effect of increasing the initial concentration of hydrogen peroxide is to increase the rate of oxidation of the indigosol (Fig. 5). For a large part of the reaction the disappearance of vat ester is of the first order. Over the range of concentrations used, the first-order rate constants for the indigo derivative are proportional to the initial concentration of hydrogen peroxide (Table II)*.

TABLE II

Oxidation of Vat Ester of Indigotetrasulphonic Acid ($6{\cdot}5 \times 10^{-5}$M.) with Hydrogen Peroxide in 0·5N. Hydrochloric Acid at 25°C.

$10^4[H_2O_2]$, moles/litre ...	2·4	2·12	1·14	0·32
$10^3 k_1$, min.$^{-1}$	7·97	7·42	3·6	1·13
$10^3 k_2$ (= $k_1/[HNO_2]$) ...	3·32	3·5	3·23	3·54

It can be seen from Fig. 6 that the effect of ferrous iron is to increase the initial rate of oxidation. This is undoubtedly due to the rapid formation of hydroxyl radicals from hydrogen peroxide by the action of ferrous iron[7, 8]. However, since ferrous iron also causes the decomposition of hydrogen peroxide to oxygen[14], the rate of oxidation of vat ester subsequently falls to a very low value.

* Hydrogen peroxide used in experiments with the indigo derivative had been stored in a brown glass bottle. There is some evidence, to be given more fully in a later paper, that a constituent of the glass interfered with the reactions.

2. REACTIONS IN A VACUUM

Apparatus and Method

Since the passage of nitrogen did not remove oxygen completely from the reaction solutions, more thorough removal by evacuation was employed. Other work in the laboratory had shown that this was a more effective way of removing dissolved air. The apparatus is shown in Fig. 8. Solutions of the reactants were filled into separate flasks *A* of 250 ml. capacity, with vacuum tap T_1 and B.14 cone joint. Not more than 100 ml. of solution was placed in each flask. The solutions were then frozen by immersing the flasks in a mixture of solid carbon dioxide and acetone, and, whilst the contents were still frozen, the flasks were evacuated (ca. 5×10^{-3} mm. of mercury). T_1 was then closed, and the solution allowed to thaw. The complete cycle was repeated three times, and the flasks were left closed.

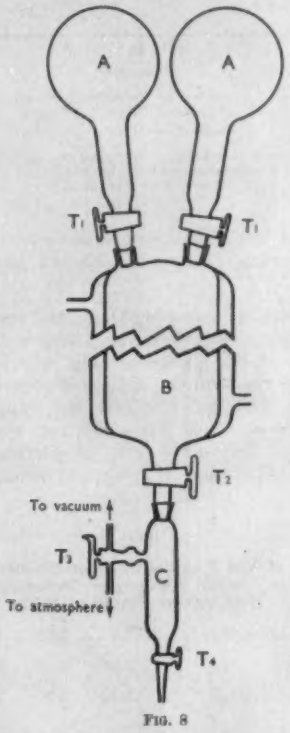


FIG. 8

The flasks were then fitted to the ground-glass sockets of the vessel *B*, which was clamped in an inverted position with the flasks immersed in a thermostat bath, water from which was circulated also through the jacket of *B*. To start the reaction, *B* was evacuated through T_2, which was then closed, T_1 opened, and the vessel restored to the upright position. The reactant solutions ran into *B*, and were mixed, after closing T_1, by gentle shaking. The draw-off vessel *C* was then fitted to the ground-glass cone at the base of *B*. To withdraw samples for analysis, *C* was evacuated through T_3, and sufficient solution was run into *C* and, after opening T_3 to the atmosphere, out through T_4.

The vat ester of anthraquinone-2-sulphonic acid was oxidised with hydrogen peroxide in this apparatus. The initial concentration of hydrogen peroxide was varied between zero (for measurements of rate of hydrolysis) and 5×10^{-3} M. Experiments were carried out at 25°C. and 50°C. in 0·033 N. and again in 0·57 N. hydrochloric acid. Light was excluded.

(*a*) *Effect of Hydrogen Peroxide*

From Fig. 9 and 10 it can be seen that the rate of formation of analytical quinone by oxidation is always greater than the rate of formation of analytical quinol by hydrolysis (i.e. when the concentration of hydrogen peroxide is zero). It must therefore be concluded that hydrogen peroxide (or an entity produced from it) reacts directly with the ester groups in the vat ester in addition to oxidising the hydroxyl groups exposed by hydrolysis.

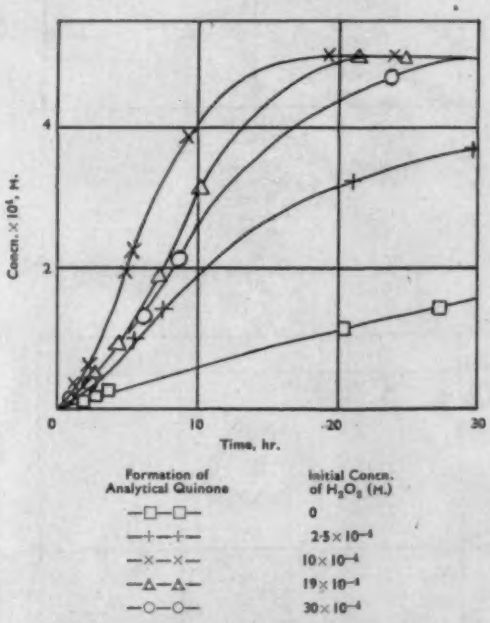


FIG. 9—Oxidation of the Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4} M.) with Hydrogen Peroxide in 0·57 N. Hydrochloric Acid at 25°C.

The rate of formation of analytical quinone passes through a maximum as the initial concentration of hydrogen peroxide is increased. It therefore appears that, in addition to the oxidation of vat ester another reaction is consuming hydrogen peroxide. This competing reaction gains in importance as the initial concentration of hydrogen peroxide is increased.

TABLE III

Oxidation of Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4}M.) with Hydrogen Peroxide in Hydrochloric Acid

HCl (N.)	Temp. (°C.)	$10^4[H_2O_2]$ (M.)	10^4k_1 (min.$^{-1}$)
0·033	25	7·0	4·9
		12·0	9·02
		13·0	7·68
		50·0	7·85
		600·0	5·38
0·033	50	0·0	10·4
		19·0	126·6
0·57	25	0·0	2·3
		2·5	9·05
		10·0	49·1
		19·0	49·1
		30·0	20·0
0·57	50	0·0	49·1
		2·5	103·6
		19·0	345·3
		500·0	207·3

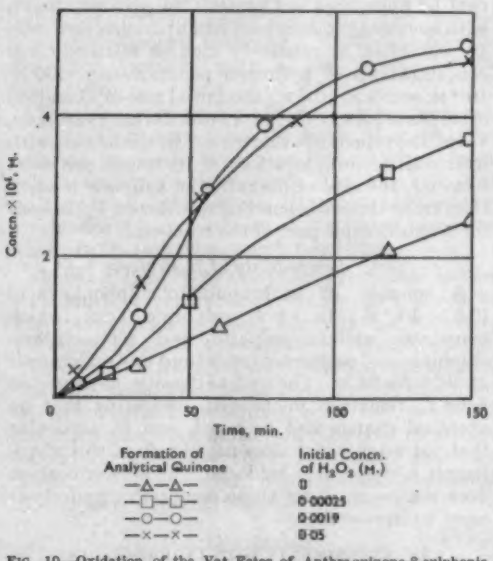


FIG. 10—Oxidation of the Vat Ester of Anthraquinone-2-sulphonic Acid (5×10^{-4}M.) with Hydrogen Peroxide in 0·57N. Hydrochloric Acid at 50°C.

Plots of log $(a-x)$ against time, where a is the initial concentration of vat ester at time $t = 0$ and x is the concentration of analytical quinone at time t, are linear except for the early slow stage of the reaction. Similar curves for hydrolysis are also linear. The vat ester reaction, for either hydrolysis or oxidation, is therefore of the first order if it is assumed that the concentration of analytical quinone is the sum of the concentrations of all species derived from vat ester, i.e. that $(a-x)$ = concentration of unchanged vat ester at time t. Values of the first-order rate constants are given in Table III. The constants for oxidations pass through a maximum with increasing concentration of hydrogen peroxide (at constant temperature and acid concentration), as expected from Fig. 9 and 10. The first-order constants for hydrolysis are approximately proportional to the square root of the acid concentration.

(*b*) *Action of Catalysts*

In further experiments, either hydroquinone or quinhydrone was added to the reactants, the molar concentration being 10% of the molar concentration of vat ester. In each case the results were very similar to those obtained in the presence of ferrous iron (Fig. 6). As compared with the uncatalysed reaction, the initial rate was considerably increased, but the formation of analytical quinone ceased after about 10% of the vat ester had reacted. At this point it was found that all the hydrogen peroxide had been decomposed.

(*c*) *Relation between Analytical Quinone, Hydrogen Peroxide, and Sulphate Ions*

A selection of the results, chosen from the extremes of rates, is given in Fig. 11. At any time during the reaction the concentration of analytical quinone is greater than either the diminution in concentration of hydrogen peroxide or the equivalent concentration of sulphate ions liberated. However, the consumption of hydrogen peroxide is, within the limits of the experimental error, equivalent to the liberation of sulphate except at very high concentrations of hydrogen peroxide. Under these conditions the consumption of hydrogen peroxide is much greater than that calculated from the expected stoichiometry, and it appears that hydrogen peroxide is being consumed by a reaction other than the oxidation of vat ester.

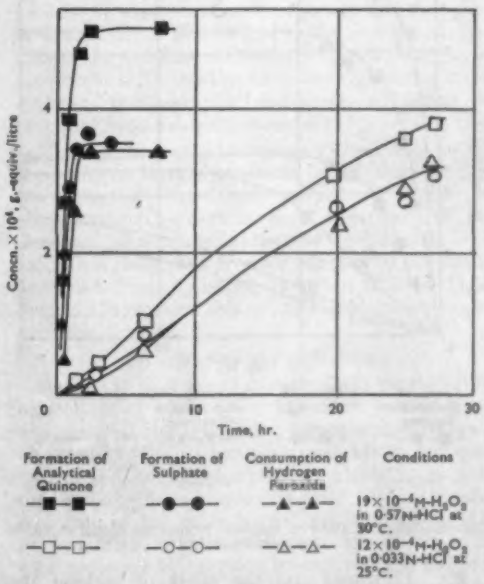


FIG. 11—Relation between Rate of Formation of Analytical Quinone and Sulphate and Rate of Consumption of Hydrogen Peroxide (initial concn. of vat ester 5×10^{-4}M.)

The relation between the consumption of hydrogen peroxide and the corresponding liberation of sulphate indicates that the sulphate groups are removed by oxidation. However, since the concentration of analytical quinone exceeds the equivalent concentration of sulphate liberated, it follows that some intermediate must be present and must contribute to the value obtained for analytical quinone. The intermediate must be produced by loss of only one sulphate group per vat ester molecule, since, because of the equivalence between hydrogen peroxide and sulphate, any molecules which have lost both sulphate groups can be present only as true, as distinct from analytical, quinone. A further consequence of the relation between hydrogen peroxide and sulphate is that the intermediate must have been produced from the vat ester by univalent oxidation, i.e. it must be at the semi-quinone level.

If the oxidation is continued, the concentration of analytical quinone reaches the value which would be expected if all the vat ester had been oxidised to true quinone. It then remains constant, although hydrogen peroxide is still present in the solution. At the same time the concentration of liberated sulphate becomes constant at a lower value than that expected on the same assumption (Fig. 12). This indicates that the intermediate, represented by the difference between the concentrations of analytical quinone and sulphate, behaves in the determination of analytical quinone as if it were actual quinone. It appears that the intermediate is stable under the conditions of the reaction.

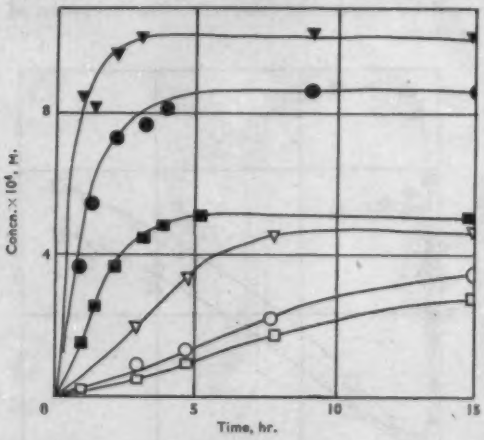


FIG. 12—Effect of Alkali on Sulphate Elimination (initial concn. of vat ester 5×10^{-4}M.)

Fig. 12 shows also the effect of making the solution alkaline with sodium hydroxide during the course of a reaction. It was found that this caused the liberation of more sulphate ions. In addition, this reaction could take place when the reaction in acid appeared to have ceased. Since the vat ester does not react in alkaline solution, the reaction must be that of an intermediate compound containing only one sulphate group. These determinations were carried out by treating 5 ml. of reaction solution with 5 ml. of 1·0 N. sodium hydroxide. After 5 min., 5 ml. of this solution was added to 5 ml. of the standard barium chloride solution, followed by 2 N. hydrochloric acid to the Methyl Red end-point. The sulphate analysis was then continued in the normal way.

(*d*) *Relative Rates of Hydrolysis and Oxidation from Sulphate Data*

The determination of analytical quinone (or quinol) is subject to interference from intermediate compounds. A comparison of the relative rates of oxidation and hydrolysis will, therefore, be more revealing when based on the determination of sulphate, which is unambiguous. The rate of liberation of sulphate by oxidation is greater than that by hydrolysis and passes through a maximum with increasing concentration of hydrogen peroxide. In particular, at relatively high or relatively low concentrations of hydrogen peroxide (e.g. 500×10^{-4} M. or $2{\cdot}5 \times 10^{-4}$ M.) the initial rate of liberation of sulphate is twice the initial rate during hydrolysis. Later, the ratio is less than this. In oxidations with intermediate concentrations of hydrogen peroxide, however, the rate of liberation of sulphate is more than twice the corresponding rate during hydrolysis for a considerable part of the reaction.

(*e*) *Reversibility of Hydrolysis*

A solution of anthraquinol-2-sulphonic acid ($2{\cdot}5 \times 10^{-4}$ M.) in 1·0 N. sulphuric acid (which contained sodium sulphite and formamidine-sulphinic acid to prevent oxidation) was maintained at 50°C. for 24 hr. The optical density, measured at 5460 A., remained unchanged, indicating that no chemical change had occurred, and in particular that vat ester, which does not absorb at this wavelength, had not been produced. Since esterification does not occur under these conditions, hydrolysis must be irreversible.

3. EXPERIMENTS WITH INDIGOSOL O4B

In addition to those already recorded, the following observations were made. They are significant when taken in conjunction with the results of the kinetic experiments described in the preceding section.

When Indigosol O4B was oxidised slowly, the solution first turned dark green, and then a green precipitate was formed which slowly became blue. A similar green precipitate was formed on simply acidifying a vat ester solution. On the supposition that the green compound was an intermediate in the oxidation of Indigosol O4B to tetrabromo-indigo, it was prepared and examined more carefully.

(*a*) *Preparation*

Purified Indigosol O4B (0·563 g.) was dissolved in boiled-out distilled water (20 ml.), and hydrogen

peroxide (2-vol., 1·6 ml.) and hydrochloric acid (4 N., 20 ml.) were added (molar ratio of indigosol : hydrogen peroxide = 2 : 1). On heating, a copious dark green precipitate was rapidly produced. It was filtered rapidly, and washed on the filter with water, dilute hydrochloric acid, dilute sodium hydroxide, and finally water. The filtrate and the washings yielded 0·2046 g. of barium sulphate, corresponding to 61·07% of the original combined sulphate of the indigosol.

(*b*) *Properties*

The precipitate was insoluble in water and dilute acids. It was slightly soluble in dilute sodium hydroxide solution. With acetone, ethanol, or pyridine the precipitate at once became blue. On oxidation, by boiling with either acidic or alkaline hydrogen peroxide or, more readily, with nitrous acid, the colour changed to blue and sulphate was eliminated. 0·158 g. of the green precipitate gave rise to 0·032 g. of barium sulphate and 0·1243 g. of blue precipitate. On reduction with either alkaline sodium hydrosulphite or an acidic solution of sodium sulphite and formamidinesulphinic acid, the green compound dissolved to give clear yellow solutions. Re-oxidation with hydrogen peroxide gave a blue precipitate in each case.

The blue precipitates obtained above were not completely characterised. However, they could be reduced in alkali to give yellow solutions, from which cotton could be dyed. The blue dye was re-formed in the usual way by atmospheric oxidation, giving dyeings of the same shade as those from authentic tetrabromoindigo.

Thus, it seems that the green precipitate can be oxidised to a vat dye and can also be reduced to the corresponding leuco compound. It must, therefore, be at the semiquinone level of oxidation. The results of the sulphate determinations suggest that the green precipitate is an impure specimen of a compound containing only one combined sulphate group per indigo residue. The formation of compounds of this type by incomplete oxidation would explain the apparently high yields obtained in the early experiments with commercial dyes.

Discussion

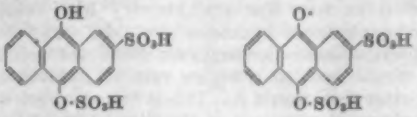
1. OXIDATIONS WITH HYDROGEN PEROXIDE

The discussion in this section is confined to the results obtained with the anthraquinone derivative, since the data for the indigo derivative are insufficient.

(*a*) *Conclusions from Experimental Results*

It has been established that oxidation of a vat ester with hydrogen peroxide occurs only under acidic conditions, i.e. under conditions where slower hydrolysis also takes place. This may be a coincidence, but the S-shaped rate-of-oxidation curves support the assumption that an initial slow hydrolysis is necessary before the main oxidation can occur. Further evidence for this assumption is provided by the action of hydroquinone and quinhydrone, which are, respectively, simple representatives of the products of hydrolysis and of hydrolysis followed by univalent oxidation. Both compounds increase the initial rate of oxidation of the vat ester of anthraquinone-2-sulphonic acid.

It is likely, from the results obtained, that hydrolysis occurs mainly to the mono-ester stage (III), further hydrolysis of this to the quinol being too slow to be significant. This is in accordance with the results of Burkhardt *et al.*[15] for the rate of hydrolysis of a number of substituted phenyl sulphates.



(III) (IV)

Since only about 70% of the original combined sulphate is eliminated by oxidation with hydrogen peroxide, even when all the vat ester has reacted, it follows that the main product of this reaction is a monosulphated derivative. This derivative is less stable in alkaline solutions of hydrogen peroxide than in acidic solutions, as is shown by the elimination of further sulphate by the action of sodium hydroxide.

The relations between (i) the consumption of hydrogen peroxide, (ii) the formation of analytical quinone, and (iii) the liberation of sulphate ions strongly suggest that the main product of the reaction is formed from the vat ester by univalent oxidation. Further support is given by the properties of the green precipitate produced from Indigosol O4B. A semiquinone ester (e.g. IV) is, therefore, proposed as the first oxidation product. That this compound is stable in acid and unstable in alkaline solutions of hydrogen peroxide may be because it exists almost completely as a valence-saturated dimer in acid and as the monomeric free radical in alkaline solutions. This would be in agreement with the known behaviour of the semiquinone produced by univalent oxidation of phenanthraquinol-3-sulphonic acid[16].

If all of the vat ester were oxidised only to the semiquinone level represented by IV, only 50% of the original combined sulphate would be eliminated. The results show that part of the semiquinone must be oxidised to the quinone. This oxidation must, however, be effected by an entity produced from hydrogen peroxide (OH or O_2H) during the reaction and not by molecular hydrogen peroxide.

(*b*) *Mechanism of Reaction*

Assuming that the monoester (III), produced by hydrolysis of part of the vat ester, causes direct oxidation of the remainder, two alternatives may be considered— (i) for each molecule of vat ester hydrolysed to the monoester, which is in turn oxidised to the semiquinone ester (IV), a further molecule of vat ester is oxidised directly to (IV) or, less often, (IV) is oxidised to the quinone; (ii) each molecule of vat ester hydrolysed and oxidised to (IV) initiates an oxidation process in which several molecules are directly oxidised.

In a reaction of type (i) the liberation of one sulphate ion by hydrolysis leads to the liberation of a second by oxidation, so that initially—

$$\frac{d[SO_4^{2-}]_{ox}}{dt} = 2\,\frac{d[SO_4^{2-}]_{hydrol}}{dt}$$

In a reaction of type (ii)—

$$\frac{d[SO_4^{2-}]_{ox}}{dt} > 2\,\frac{d[SO_4^{2-}]_{hydrol}}{dt}$$

for a considerable part of the reaction.

It will be seen that the requirements for (i) are fulfilled at very low and at very high relative concentrations of hydrogen peroxide, and for (ii) at intermediate concentrations. Moreover, reaction (ii) would lead to a higher rate of oxidation of vat ester than would (i). This is in agreement with the observed variation in the rate constants with increasing concentration of hydrogen peroxide.

The autoxidation of quinols proceeds through the intermediate formation of free radicals[17], and in acidic oxidations by hydrogen peroxide the radicals OH and O_2H are always produced[7, 8]. In addition, the curve representing the oxidation of vat ester with hydrogen peroxide catalysed by hydroquinone is very similar to that catalysed by ferrous iron. This is known to produce both OH and O_2H from the peroxide[14].

It is reasonable to assume, therefore, that the first reaction between a quinol and hydrogen peroxide is analogous to the reaction with ferrous iron and leads to the formation of a hydroxyl radical and a semiquinone. If the monoester (III) catalyses the oxidation of vat ester by virtue of the phenolic hydroxy group exposed by hydrolysis, a similar reaction will occur here also. Subsequent reactions of the hydroxyl radical will depend on the relative concentrations of the reactants.

With these considerations in mind, the changes which may occur in the system vat ester–hydrogen peroxide–acid will be discussed in terms of the reactions shown in the scheme V.

Reactions (1), (2), and (11) will always occur. Reactions (4) and (5) are known to occur in solutions of hydrogen peroxide[8, 14], and Reaction (8) is considered to be likely[18]. The relative importance of the various reactions at different concentrations of hydrogen peroxide may now be discussed.

(i) Very Low Concentrations of Hydrogen Peroxide

Reaction (4), and hence reactions of O_2H, will largely be suppressed and OH will react according to (3). Reaction (9) will make only a small contribution, since the concentration of mono-ester (III) is small compared with that of vat ester. The contribution of (10) will depend on the equilibrium position of (11), which, from the experimental observations, must be assumed to favour the formation of dimer. The main sequence is, therefore, (1) → (2) → (3). Thus, if (2) and (3) are rapid (which is essential to explain the experimental results), the overall rate of formation of sulphate ions will be, initially, twice that of Reaction (1).

(ii) Very High Concentrations of Hydrogen Peroxide

Reaction (3) will now be replaced largely by (4), thus leading to the formation of O_2H. Reaction (5) will occur in preference to (6), and (4) and (5) together will constitute a chain decomposition of hydrogen peroxide. The main chain-stopping reaction will be (3), since (9) and (10) have already been excluded. The main sequence, therefore, is (1) → (2) → $(4, 5)_n$ → 3, and the relation between the rates of formation of sulphate ions will be the same as in (i).

(iii) Intermediate Concentrations of Hydrogen Peroxide

When the concentration is not so high that (6) is excluded in favour of (5), but high enough to permit (4), the sequence (6) → (7) → (8) → (4) can occur and form a reaction chain. Chain-stopping, as before, will be largely by (3). The main sequence, therefore, is (1) → (2) → $(4, 6, 7, 8)_n$ → (3). With this mechanism, the rate of oxidation will be more than twice the rate of hydrolysis.

V— The System Vat Ester–Hydrogen Peroxide–Acid

$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + H_2O$	$\xrightarrow{H^+}$	$HO{-}A{-}O{\cdot}SO_3H + H_2SO_4$	(1)
$HO{-}A{-}O{\cdot}SO_3H + H_2O_2$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2O + OH$	(2)
$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + OH$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2SO_4$	(3)
$H_2O_2 + OH$	⟶	$H_2O + O_2H$	(4)
$H_2O_2 + O_2^-$	⟶	$O_2 + OH^- + OH$	(5)
$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + HO_2$	⟶	$HO{\cdot}O{-}A{-}O{\cdot}SO_3H + HSO_4\bullet$	(6)
$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + HO{\cdot}O{-}A{-}O{\cdot}SO_3H$	⟶	$2\bullet O{-}A{-}O{\cdot}SO_3H + H_2SO_4$	(7)
$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + HO_2$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2SO_5$	(6a)
$HO_3S{\cdot}O{-}A{-}O{\cdot}SO_3H + H_2SO_5$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2SO_4 + HSO_4\bullet$	(7a)
$HSO_4\bullet + H_2O$	⟶	$H_2SO_4 + OH$	(8)
$HO{-}A{-}O{\cdot}SO_3H + OH$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2O$	(9)
$\bullet O{-}A{-}O{\cdot}SO_3H + OH$	⟶	$\bullet O{-}A{-}O\bullet\,(O{=}A{=}O) + H_2SO_4$	(10)
$2\bullet O{-}A{-}O{\cdot}SO_3H$	⇌	Dimer	(11)
$HO{-}A{-}O{\cdot}SO_3H + HO_2$	⟶	$\bullet O{-}A{-}O{\cdot}SO_3H + H_2O_2$	(12)

A =

Reactions 6(*a*) and 7(*a*) together may be substituted for (6) and (7) without affecting the preceding arguments. Reaction (12) must also be considered, but it will not make an important contribution, since O_2H will be competing for the mono-ester with the hydrogen peroxide present at a higher concentration.

The results of passing from mechanism (i) through (iii) to (ii), as the initial concentration of hydrogen peroxide is increased, are thus in accordance with the experimental observations. When the concentration of hydrogen peroxide is varied over a small range only and is of the same order as that of vat ester, so that mechanism (i) alone has to be considered, the rate of oxidation will be proportional to the concentration of hydrogen peroxide. This has been observed with the vat ester of indigotetrasulphonic acid (Table II).

Reaction (5) is represented as one of the anion of O_2H (O_2^-). The existence of O_2^- and its reaction by (5) are thought to be very likely [8]. The anion is a reducing agent, whereas the undissociated radical is an oxidising agent (as in Reaction 6).

The fact that Indigosol O4B can be oxidised with ammonium persulphate, and that the reaction is catalysed by ferrous iron, is evidence that the reactions of the bisulphate radical shown in (8) can take place or are likely to take place. Persulphates are thought to produce bisulphate radicals by reaction with ferrous iron, and these in turn may liberate hydroxyl radicals from water [18].

(*c*) *Conclusion*

Whilst the reaction mechanisms which have been suggested must still be regarded as tentative, the following main characteristics may be deduced—(i) The vat ester is slowly hydrolysed in acid, in the absence of oxidising agents, chiefly to the mono-ester (III). (ii) Direct oxidation of vat ester with hydrogen peroxide is initiated by the monoester, the first oxidation product being the semiquinone ester (IV). (iii) The semiquinone ester (IV) is not readily oxidised further by molecular hydrogen peroxide, but may be oxidised by radicals (OH and O_2H) produced during the reaction.

With the indigo derivative it appears that larger quantities of the fully oxidised (i.e. quinone) form are produced. This may be due to the semiquinone ester being less stable than that in the anthraquinone series. Further examples of almost complete oxidation of indigoid vat esters by the action of hydrogen peroxide will be presented in a later paper.

2. OXIDATIONS WITH NITROUS ACID

From the known behaviour of nitrous acid it is likely that oxidation is effected by the nitrosyl anion NO^+. This is produced directly from nitrous acid without the intervention of hydrolysis products from the vat ester. Oxidations with nitrous acid are not, therefore, governed by the rate of hydrolysis, and are in fact more rapid than oxidations with hydrogen peroxide, which are so governed.

The anion NO^+ causes a univalent oxidation only, so that semiquinone derivatives of type IV should be formed and represent the intermediate product whose existence is indicated by the experimental results (Fig. 2). However, oxidation of the semiquinone ester to the vat dye will occur owing to the independent formation of NO^+.

The effect of oxygen, which produces an irregularity in the consumption of nitrous acid, is of interest and will be examined in more detail at a later date. The simplest explanation is that nitrous acid is being regenerated by the sequence of reactions given in VI, until all oxygen has been removed from the system. At this stage, the reaction between nitrous acid and vat ester should be normal. The rate-of-reaction curves after the irregularity in the curve for nitrous acid appear to confirm this assumption.

$$\begin{aligned} NO^+ + e^- &\longrightarrow NO \\ 2NO + O_2 &\longrightarrow N_2O_4 \\ N_2O_4 + H_2O &\longrightarrow HNO_2 + HNO_3 \end{aligned}$$
(VI)

The oxidation of formic acid with nitrous acid has recently been studied by Longstaff and Singer [11]. Their conditions were very similar to those of the present work, and they did not claim to have removed oxygen completely. Nevertheless, they found that the reaction was of the first order with respect to nitrous acid from the beginning, with no interference from oxygen. If this is correct, it suggests that the effect of oxygen observed during the present work comes from interaction between oxygen, vat ester, and nitrous acid (or an entity produced from it). We have observed, however, that the spontaneous decomposition of nitrous acid also follows an irregular course in the presence of traces of oxygen.

Whatever the explanation, the apparent re-formation of nitrous acid and the accompanying increase in the rate of oxidation of the vat ester will undoubtedly play their part during development under normal industrial conditions.

3. ATMOSPHERIC OXIDATION

Atmospheric oxidation is likely to occur at any time unless protective reducing agents or alkalis are present. It will be recalled that an entity capable of oxidising the iodide ion to iodine is produced by the action of air on an acidified indigosol solution (Fig. 7). This could be explained by the reactions VII, i.e. that the radicals OH and O_2H are formed. Reactions shown in V could then follow. The reaction will be autocatalytic owing to the liberation of sodium bisulphate and the subsequent increase in acidity.

$$\begin{aligned} HO\text{-}A\text{-}O\cdot SO_3H + O_2 &\rightarrow {}^{\cdot}O\text{-}A\text{-}O\cdot SO_3H + HO_2 \\ HO\text{-}A\text{-}O\cdot SO_3H + HO_2 &\rightarrow {}^{\cdot}O\text{-}A\text{-}O\cdot SO_3H + H_2O_2 \end{aligned}$$
(VII)

Autoxidation leading to the formation of semiquinone derivatives affords a plausible explanation for the shape of the curves obtained by El Borai and Turner in their study of the diffusion of vat esters from a starch phase to cellulose during steaming [19]. To explain the

appearance of maxima on the rate-of-diffusion curves, they suggested that vat ester was being decomposed, in the steamer, to a compound of different solubility and diffusion coefficient. This compound was nevertheless analysed as vat ester by their method, viz. development to the vat dye with nitrous acid. Since in their experiments no precautions were taken to remove oxygen from mains steam, the possibility of autoxidation was very great. The formation of a semiquinone derivative under these conditions is, therefore, very likely. This would satisfy their requirement for the production of an intermediate compound which would still be oxidised to the vat dye with nitrous acid.

4. CONCLUSIONS

The results reported in this paper represent an initial survey of part of the chemistry of esters of leuco vat dyes. They show that these esters do not react in a simple way and may react differently with different oxidising agents. The types of reaction which may occur with hydrogen peroxide have been indicated but not proved conclusively. Work is continuing, particularly in regard to the the properties of the monoester and semiquinone ester.

* * *

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DEPARTMENT OF TEXTILE CHEMISTRY
COLLEGE OF TECHNOLOGY
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The Dyeing of Acetate Rayon with Disperse Dyes
IV—Adsorption Isotherms

C. L. BIRD and F. MANCHESTER

Equilibrium isotherms have been obtained at 80°C. with acetate rayon and five disperse dyes. Two azo dyes showed a linear relationship up to saturation between dye on the fibre and dye in the aqueous phase. Non-linear curves were obtained with three anthraquinonoid dyes, but a straight line was obtained when a solubilisate of 1-methylamino-4-anilinoanthraquinone was used in place of a dispersion. With purified Dispersol Fast Scarlet B the slope of the isotherm was found to be independent of liquor : yarn ratio, and inversely proportional to the concentration of dispersing agent over a limited range.

The adsorption by acetate rayon of purified Lissapols C and LS has been studied at 80°C. Both detergents hydrolyse gradually in hot aqueous solution.

INTRODUCTION

During the past thirty years a number of papers have described equilibrium dyeings of disperse dyes and related compounds on acetate rayon.

Meyer, Schuster, and Bülow[1] studied the partition of *p*-nitroaniline between cellulose acetate and water at room temperature over the concentration range in water of 0–180 mg./litre and found a constant partition ratio of 182.

Brandenburger[2] applied four partly purified disperse dyes of undisclosed constitution to acetate rayon at 65°C. in presence of soap. On plotting dye on the fibre against dye in the residual dyebath a straight line was obtained in each case. The report of this work contains very few experimental details.

Burns and Wood[3] applied pure 1-amino-, 2-amino-, and 1:4-diamino-anthraquinone to acetate rayon at 26°C. for 8 days. The adsorption isotherms obtained were of the Freundlich type, but the technique used by these authors was unsatisfactory, and their results are open to question.

Kartaschoff and Farine[4] measured the distribution of a number of pure anthraquinonoid disperse dyes at 60°C. between cellulose acetate and ethanol. A constant partition was found, but the dye concentration varied by only about 20%. No correlation was found when the partition coefficients were compared with the ratio of saturation solubilities in the two phases.

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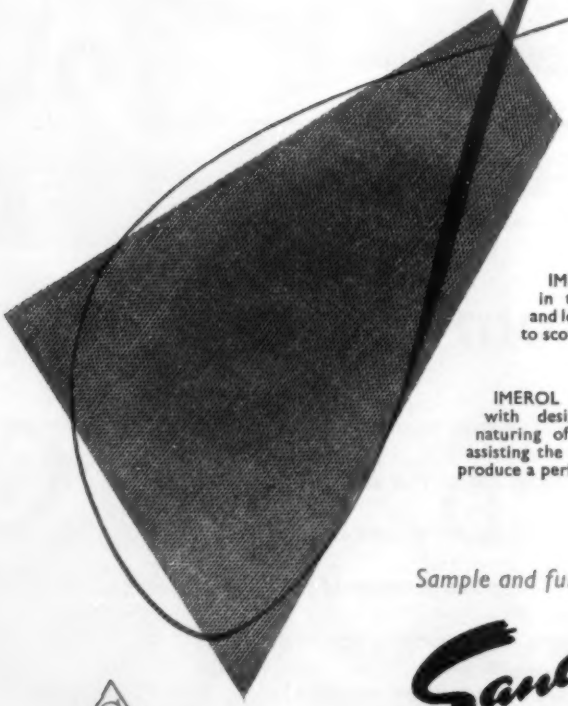

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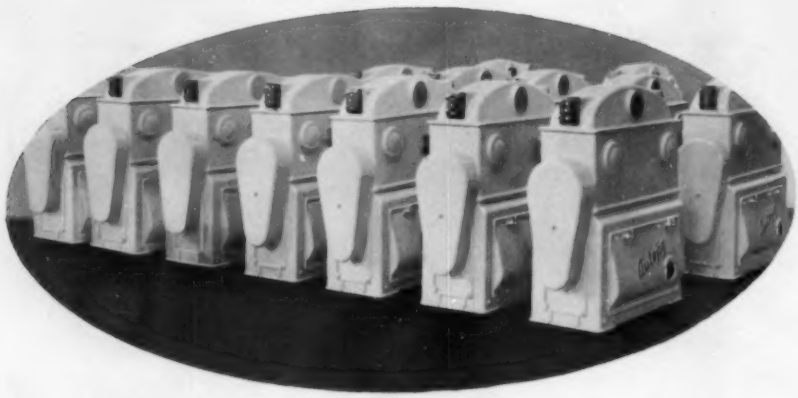

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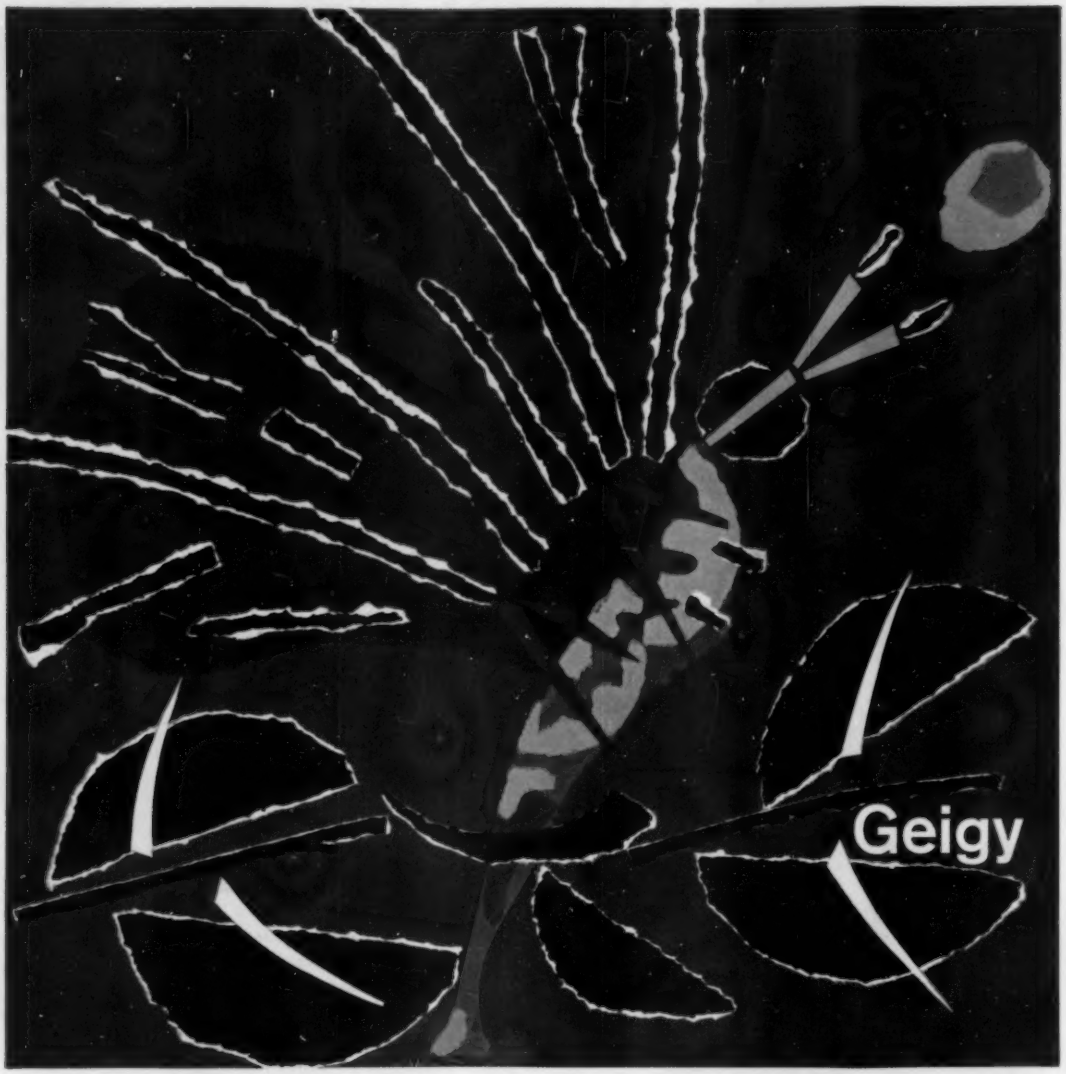

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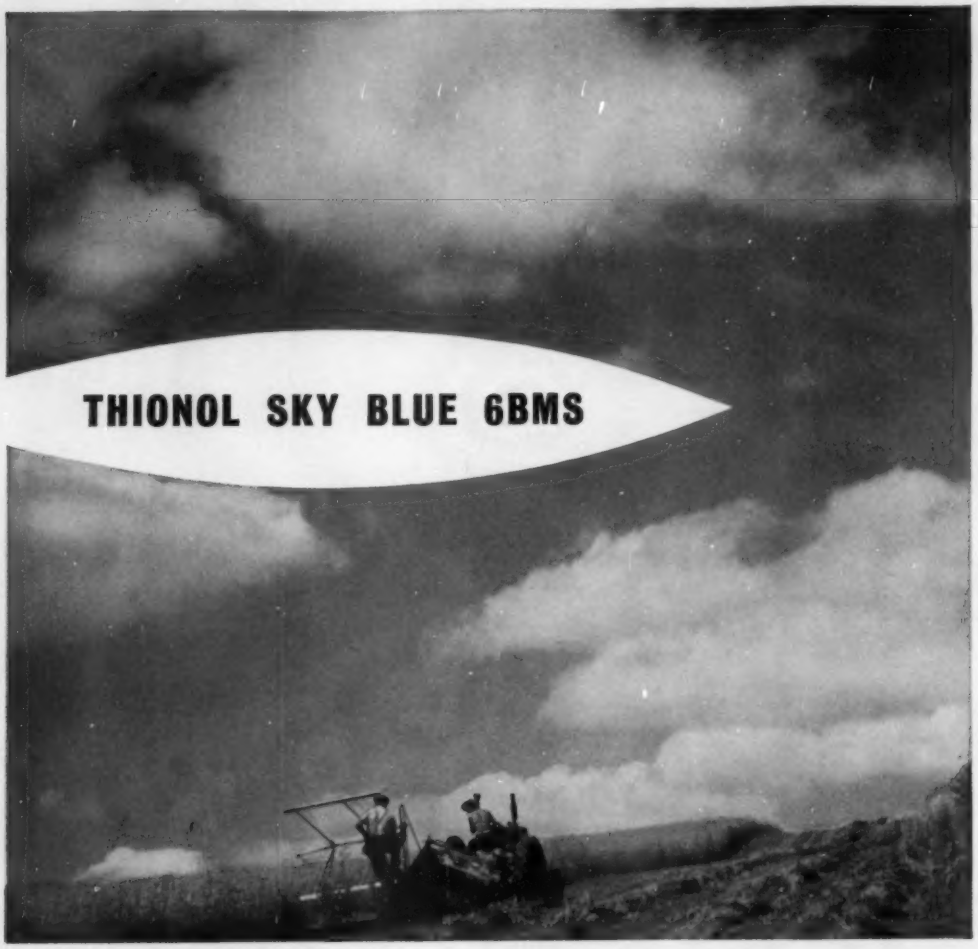

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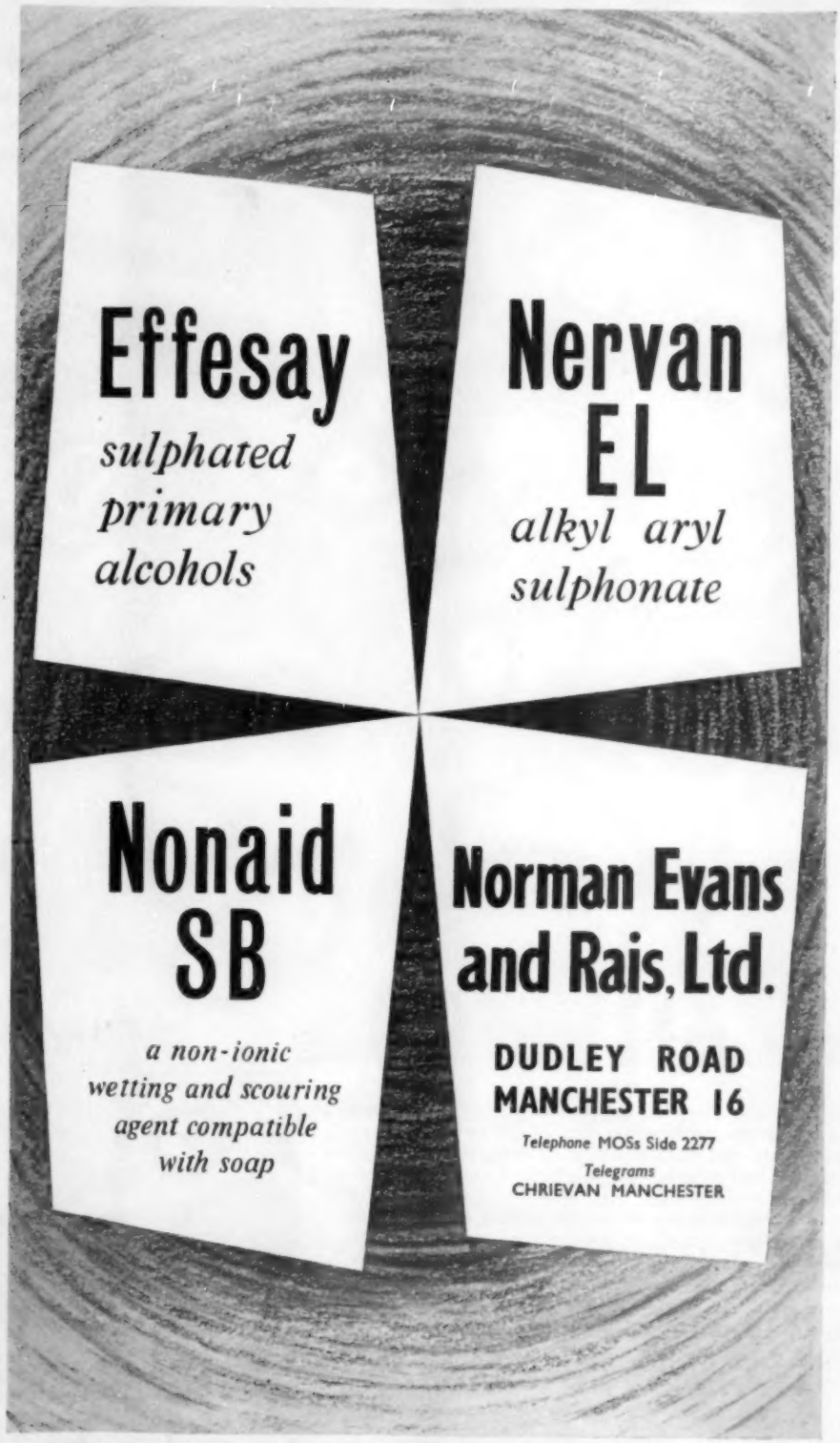
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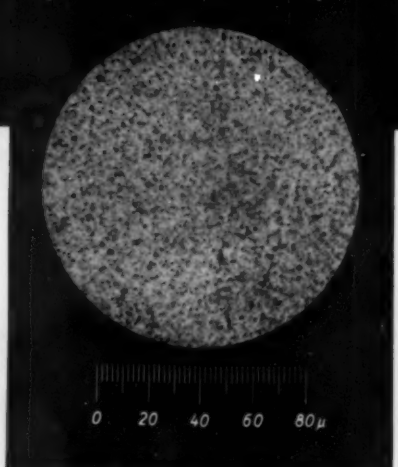

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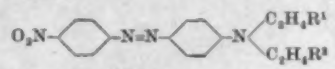
tion between acetate rayon and a dyebath at 85°C. of four related anthraquinonoid disperse dyes, viz. 1-methylamino-, 1-ethylamino-, 1-β-hydroxyethylamino-, and 1-*isobutylamino*-4-anilinoanthraquinone. Their adsorption isotherms fitted the Langmuir equation, but this result was regarded as fortuitous, as dilution of the dyebath had little effect on the amount of dye adsorbed by the fibre. They considered, however, that the shape of their isotherms ruled out the solid solution hypothesis, which requires a constant partition ratio.

Wahl, Arnould, and Simon [6] used a modified dispersion technique with a series of dyes of general formula—



where R^1 and R^2 are H, OH, $O{\cdot}C_2H_4OH$, or $O{\cdot}C_2H_4{\cdot}O{\cdot}C_2H_4OH$. They obtained a straight-line relationship between dye on the fibre and dye in the residual dyebath. Moreover, these authors showed that a point is reached when the fibre becomes saturated; the curve then becomes an almost horizontal straight line.

The same type of curve has been obtained by Daruwalla and Turner [7] for Duranol Red 2B (ICI) on cellulose acetate and for Dispersol Fast Scarlet B (ICI) on nylon, distribution being effected by steaming a cellulose acetate or nylon film in contact with a starch film containing the dye.

Schuler and Remington [8] have shown that the same linear relationship is obtained with disperse dyes and polyethylene terephthalate (Terylene). Their isotherms were for 89·3°, 100°, and 120°C., equilibrium dyeings being carried out, up to saturation, without addition of dispersing agent.

Bird, Manchester, and Harris [9] have shown that a linear partition is obtained over a considerable concentration range at 80°C. when the dye *p*-nitro-*o*-anisidine→*NN*-bis-β-hydroxyethylaniline is distributed between water and acetate rayon, the equilibrium being a reversible one.

Majury [10] has reported that *p*-nitroaniline and *p*-aminoazobenzene show a linear partition between water and cellulose acetate at 80°C. up to saturation of the aqueous phase.

Recent work therefore points to the conclusion that, when a disperse dye is distributed between acetate rayon (or nylon or Terylene) and a disperse dyebath, the equilibrium relationship corresponds to partition of the dye between two immiscible solvents. Using either water or a solution of dispersing agent of constant composition, the system is defined by the equation—

$$\frac{D_f}{D_s} = \frac{S_f}{S_s} = K$$

where D_f and D_s are the equilibrium concentrations of dye on the fibre and dye in solution in the aqueous phase, expressed as moles per kilogram of dry fibre and moles per litre respectively, S_f and S_s are the corresponding saturation values, and K (the partition coefficient) is a constant.

As Stubbs [11] has suggested, however, the point of apparent saturation of the fibre may not be the true saturation value. The fibre has a very large number of available sites and should be capable of absorbing much more dye. In practice the amount of dye which the fibre can absorb is governed by the aqueous solubility of the dye and the partition coefficient. If for a particular dye both of these values were high, the amount of dye adsorbed by the fibre would be large and the isotherm might not be linear beyond a certain point.

The work described in the present paper, which forms part of a more extensive investigation, was commenced before the publication of papers by Wahl, Arnould, and Simon [6], Daruwalla and Turner [7], Schuler and Remington [8], and Majury [10]. These authors have established the linear nature of the adsorption isotherm obtained with disperse dyes. The present work provides confirmation of their results and indicates that, contrary to the findings of Vickerstaff and Waters [5], 1-methylamino-4-anilinoanthraquinone is not an exception to the general rule.

OUTLINE OF THE INVESTIGATION

The present work describes adsorption and desorption isotherms obtained at 80°C. with acetate rayon and dispersions of the following dyes—

p-Nitroaniline→diethylaniline

p-Nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline (Dispersol Fast Scarlet B)

1-Amino-4-hydroxyanthraquinone (Duranol Red 2B)

1:4-Bismethylaminoanthraquinone (Duranol Brilliant Blue G)

1-Methylamino-4-anilinoanthraquinone

With Dispersol Fast Scarlet B the effect of varying the amount of dispersing agent has also been studied.

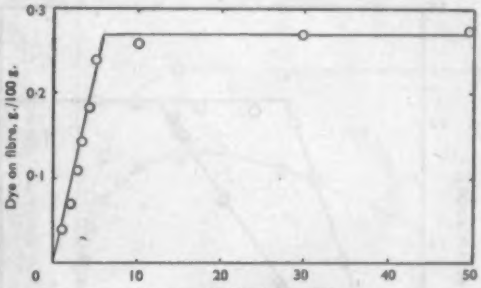


FIG. 1—*p*-Nitroaniline→diethylaniline

The results are illustrated in Fig. 1–6. Except where otherwise stated, all adsorption and desorption experiments were carried out in presence of 0·002 M. (0·946 g./litre) sodium 1-oleyl-4-anisidine-2-sulphonate.

Purified Lissapol LS (ICI) (sodium 1-oleyl-4-anisidine-2-sulphonate) was chosen as the dispersing agent rather than Lissapol C (ICI) (sodium cetyl–oleyl sulphate) because of its greater stability. Preliminary experiments showed that both compounds decompose when held in solution at 80°C.

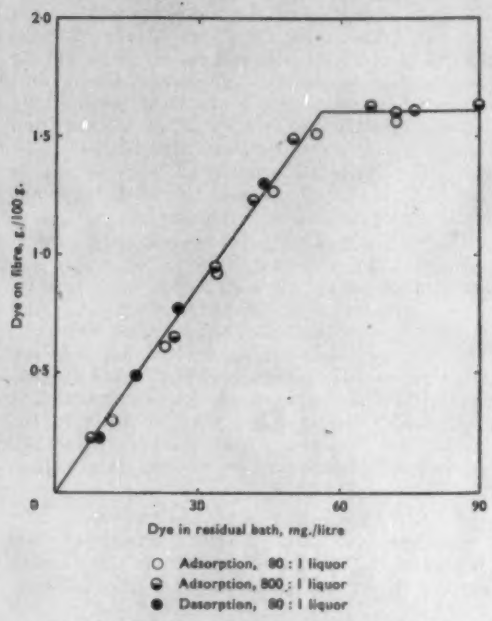


FIG. 2— *p*-Nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline

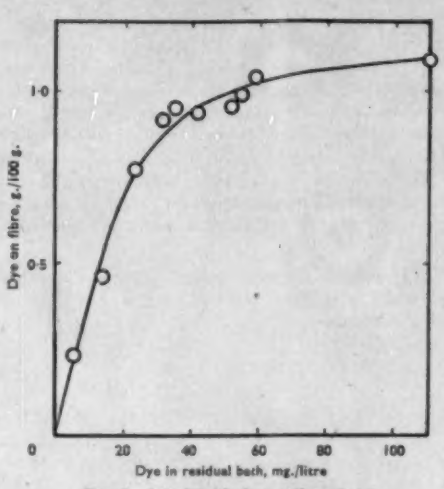


FIG. 4— 1-Amino-4-hydroxyanthraquinone

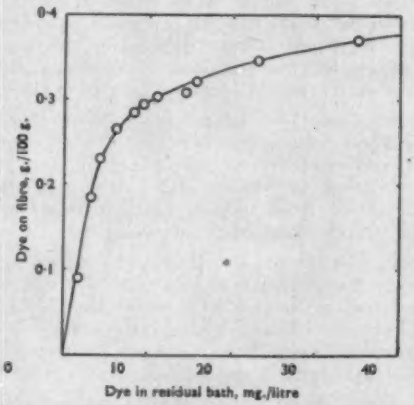


FIG. 5— 1:4-Bismethylaminoanthraquinone

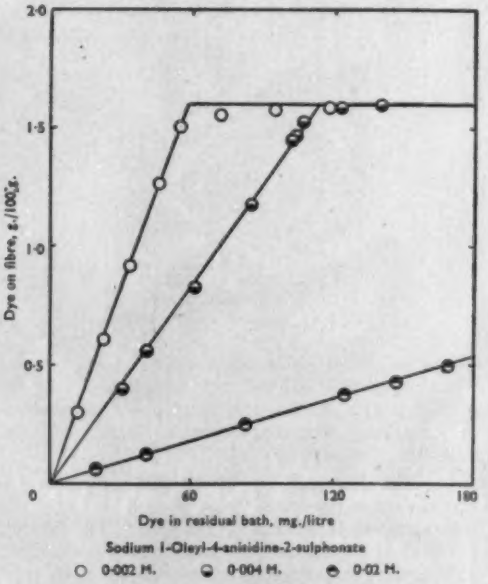


FIG. 3— *p*-Nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline

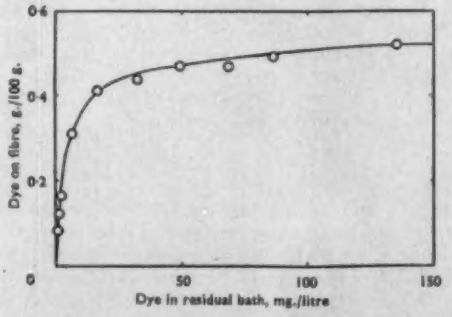


FIG. 6— 1-Methylamino-4-anilinoanthraquinone

for a prolonged period, decomposition being fairly rapid with sodium cetyl–oleyl sulphate, as shown in Table I.

The adsorption of purified Lissapols C and LS by acetate rayon at 80°C. has also been studied; the results are given in Table II.

TABLE I

Decomposition of Purified Dispersing Agents (0·01 M.) at 80°C.

Time (hr.)	Sodium Cetyl–Oleyl Sulphate		Sodium 1-Oleyl-4-anisidine-2-sulphonate	
	pH	Decomp. (%)	pH	Decomp. (%)
0	5·0	0	6·4	0
2	3·8	1	6·2	0
4	3·3	2	6·2	1
8	3·0	12	6·1	0
27	—	—	5·5	2
30	2·6	76	—	—
50	2·3	96	5·4	7
70	2·2	98	—	—
75	—	—	5·5	10
90	2·2	99	—	—
95	—	—	5·5	13

TABLE II

Adsorption of Purified Dispersing Agents by Acetate Rayon at 80°C.

(Liquor : yarn ratio 80 : 1. Time 90 min.)

Concn. (M. × 10⁴)	Amount adsorbed (millimoles/kg.) Sodium Cetyl–Oleyl Sulphate	Sodium 1-Oleyl-4-anisidine-2-sulphonate
1	0·7	0·5
2	1·3	0·6
4	3·8	1·3
6	4·6	1·4
8	5·4	1·8
10	6·3	1·8
15	7·6	—
20	7·9	—
25	8·0	—

EXPERIMENTAL

Purified dyes and dispersing agents, and solvent-extracted conditioned Celanese yarn, were prepared as described in Part I [12]; suspensions of purified dyes were prepared as described in Part III [13]. Dyeings were carried out in a modified Marney machine as before, and dye on the fibre and in the dyebath was estimated colorimetrically in the usual way, the results being expressed on the weight of conditioned yarn.

In the case of 1-methylamino-4-anilinoanthraquinone an additional isotherm was obtained with solubilised dye in place of a dispersion. The solubilised dye was prepared by stirring a 0·002 M. solution of the dispersing agent with an excess of crystalline dye under reflux at 80°C. until equilibrium had been established. The excess of solid dye was then filtered off, and the solubilisate was used in the following manner. Five 0·1-g. hanks of acetate rayon yarn were dyed at a liquor : yarn ratio of 800 : 1 in separate dyebaths for 8 hr., after which the first was removed and analysed. The remainder were dyed for a further 6 hr., and the process was repeated until the last hank had been dyed for a total of 32 hr.

Purified Lissapol LS and Lissapol C were analysed by the method of Barr, Oliver, and Stubbings [14]; the average molecular weights were found to be 473 and 308 respectively. The same method of analysis was used when estimating residual dispersing agent in the decomposition and adsorption experiments (Tables I and II), which were carried out, in a thermostat bath, in 250-ml. bottles fitted with rubber stoppers held in position by means of small springs attached to the necks of the bottles.

DISCUSSION

The possible effect of the decomposition of dispersing agent does not appear to have been considered in previous studies of disperse dyeings. The decomposition of sodium alkyl sulphates is apparently well known in technical practice, and the commercial products contain buffering and stabilising agents, which are effective for reasonable periods at elevated temperatures. Over very prolonged periods, however, it might be expected that breakdown of these stabilised products would occur, and this appears to be the explanation of some anomalous results obtained by Vickerstaff and Waters [5]. When using dispersions of 1-methylamino-4-anilinoanthraquinone in presence of commercial Lissapol C for times up to 143 hr. at 85°C., it was found that the amount of dye on the fibre was appreciably less than that obtained for short dyeing times up to 8 hr. The explanation given by these authors was that there appeared to be the possibility of a change in particle size in the dispersion, which affected the final solubility of the dye in the bath. The present explanation, illustrated by Fig. 7, appears to be more likely.

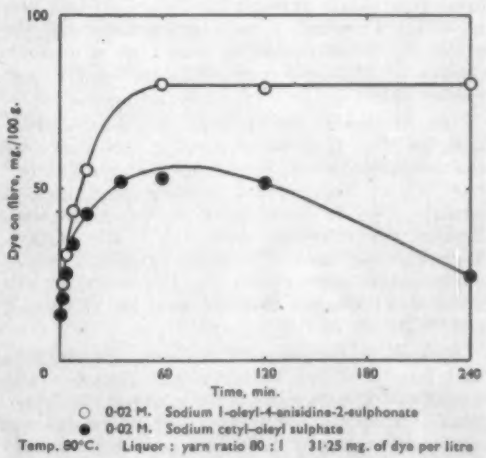


FIG. 7— Effect of Decomposition of Dispersing Agent on Dyeing of *p*-Nitroaniline→diethylaniline

Hydrolysis of the alkyl sulphate will result in the production of sodium hydrogen sulphate according to the following equation—

$$R\text{·}O\text{·}SO_2Na + H_2O \rightarrow R\text{·}OH + NaHSO_4$$

The sodium hydrogen sulphate will form a salt with the (basic) disperse dye, and so reduce the amount of dye adsorbed by the fibre.

It has been shown by Desseigne [15] that the breakdown of the higher alkyl sulphates is very sensitive to change in pH, and between pH 3 and pH 2 there is approximately a tenfold increase in the rate of decomposition for every rise of 20°C.

The maximum adsorption of sodium cetyl–oleyl sulphate by acetate rayon at 80°C. was found to be 0·8 millimole per 100 g., which is in good agreement with the value (0·75 millimole per 100 g.) obtained by Weatherburn and Bailey [16] for sodium cetyl sulphate and acetate rayon at 50°C.

The adsorption isotherms for *p*-nitroaniline→diethylaniline and *p*-nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline are similar to those obtained with the same dyes by Wahl, Arnould, and Simon [6], and it seems probable that all the azo disperse dyes give straight-line isotherms of the type illustrated in Fig. 1 and 2. The very low aqueous solubility of the former dye does not affect the shape of the curve.

The adsorption and desorption isotherms of *p*-nitroaniline→*N*-ethyl-*N*-β-hydroxyethylaniline are identical, and varying the liquor : yarn ratio does not appear to affect the slope. Varying the amount of dispersing agent (Fig. 3) alters the slope, but does not affect the linear relationship or the saturation value. These findings add further support for the now generally accepted view that disperse dyes pass through aqueous solution before being adsorbed by the fibre, the micelles of dispersing agent acting merely as a reservoir of solubilised dye. Whilst these micelles cannot penetrate the fibre, work in progress has shown that sodium 1-oleyl-4-anisidine-2-sulphonate diffuses very slowly through a cellulose acetate film at 80°C. Presumably, only single molecules are involved, diffusion taking place in a manner similar to that observed with Aerosol OT and viscose film [17].

The isotherm for 1-amino-4-hydroxyanthraquinone (Fig. 4) shows appreciable curvature near the saturation point, but Daruwalla and Turner [7] have shown that, under printing conditions, a straight line is maintained up to saturation. Similar curvature is shown by 1:4-bismethylaminoanthraquinone (Fig. 5) and 1-methylamino-4-anilinoanthraquinone (Fig. 6); the curve for the latter dye resembles that obtained by Vickerstaff and Waters [5].

Because of the shape of the isotherm obtained with 1-methylamino-4-anilinoanthraquinone, Vickerstaff and Waters rejected the solid solution hypothesis. They showed, however, that this dye was not readily taken up by the fibre unless it was very finely ground, and it seemed to us possible that the curvature was due to the presence in the system of unreactive crystalline particles (although, as Vickerstaff [18] has pointed out, a constant proportion of such particles should merely alter the slope of the isotherm). Further evidence for this view was provided by the straight-line relationship obtained in desorption experiments with this dye, our results again confirming those of Vickerstaff and Waters. Experiments were therefore carried out in which acetate rayon yarn was dyed at 80°C. in successive lots of a saturated solution (8·2 mg./litre) of 1-methylamino-4-anilinoanthraquinone in 0·002 M. sodium 1-oleyl-4-anisidine-2-sulphonate. The final hank, which had been dyed for a total of 32 hr., was in equilibrium with a nearly saturated solution of dye (8·1 mg./litre). The results are illustrated in Fig. 8, which also includes the results of desorption experiments using an 80 : 1 liquor : yarn ratio. It is seen that a straight-line reversible relationship, which is independent of liquor : yarn ratio, is obtained up to a point where the aqueous phase is almost saturated. Thus, 1-methylamino-4-anilinoanthraquinone falls into line, and it is probable that the straight-line reversible relationship applies to all disperse dyes.

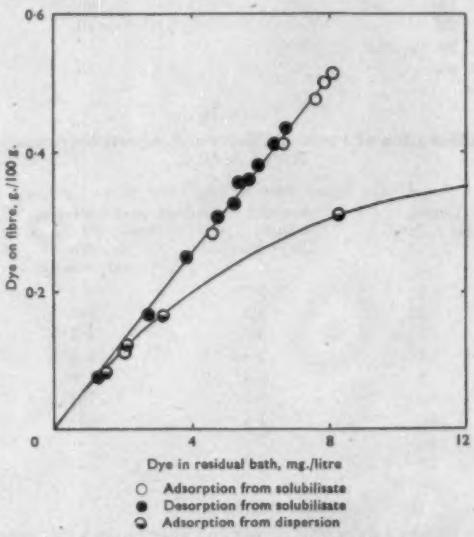


FIG. 8—1-Methylamino-4-anilinoanthraquinone

A point of practical interest illustrated in Fig. 8 is that, with dyes which do not show a linear relationship up to saturation, there is likely to be considerable waste of dye and poor building up [19] when heavy dyeings are involved. With this type of dye, also, it is of vital importance to reduce the particle size to the minimum possible value [8, 9].

DEPARTMENT OF COLOUR CHEMISTRY AND DYEING
THE UNIVERSITY
LEEDS 2

(*Received 14th April 1955*)

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CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Theories of Dyeing

Dr. Whittaker asks what knowledge is required to understand the Explanatory Papers on Modern Theory[1]. The answer is his own well known recipe for most dyeing problems—common sense and common salt!

Only common sense is needed, since the theories are simple and easy to grasp by anyone who will have the common salt or self-confidence to believe in his own ability to understand. My paper[2] may seem difficult as it is arithmetical, or because I put in something for everybody, even some subtle points for the experts, to guard against criticism from that quarter.

What I feared most was that the paper would seem superfluous because everybody would already know all it contained. I am grateful to Dr. Whittaker for assuring me how wrong I was, and I hope that others will be encouraged to complain about specific obscurities, so that I can supplement the paper by further explanations in the form of Letters to the Editor.

L. Peters

Department of Textile Industries
The University
Leeds 2

29th July 1955

[1] Whittaker, C. M., J.S.D.C., **71**, 401 (July 1955).
[2] Peters, L., *ibid.*, **71**, 174 (April 1955).

Dr. Whittaker[1] asks what standard of knowledge of physics and mathematics is required to understand modern theories of dyeing, and wonders how many practical dyers have the requisite knowledge. We must assume that they all have, for, as Dr. C. J. T. Cronshaw[2] has well said: "A chemist . . . must willingly accept as a burden of his vocation the responsibility of keeping up with his chosen subject". A first-class technologist must necessarily be a first-class scientist.

Whatever course the future tutorial activities of the Society may take—and I sincerely hope that they will continue—it would be very undesirable for it to sponsor, say, a list of textbooks of physics and mathematics, with the assurance that all that the would-be theorist has to do is to read Chapters I–XX "and you needn't bother about the bits in small print". Much guidance can be obtained from the Associateship syllabus, which will, I hope, remain fluid at least as long as does dyeing theory.

I am convinced that in our scientific activities we should cater for the "under 30s" rather than the "over 50s", even though the latter may be in the majority, for it is among the "under 30s" that we must look for future leaders in the dyeing industry. We must see to it that they do not falter through any shortcomings on our part.

As for the theory of hydrogen bonding, if it has served its purpose and has been superseded by something better, let it be discarded. To join the band of authors of discarded theories is to be in very good company indeed. We can all agree with Sir J. J. Thomson[3] that theories are the life-blood of physics, and the most potent begetters of research.

H. C. Olpin

462 Kedleston Road
Allestree
Derby

6th August 1955

[1] Whittaker, C. M., J.S.D.C., **71**, 401 (July 1955).
[2] Cronshaw, C. J. T., *Dyer*, 455 (1946).
[3] Thomson, J. J., B.B.C. lecture (1930).

"Man-made"

Dr. J. S. Heaton[1] objects to the word "man-made" as applied to synthetic fibres, and prefers the "familiar and pleasant" word "artificial".

Perhaps Dr. Heaton does not know that Webster's *New International Dictionary* (second edition, unabridged) variously defines the word "artificial" as "made or contrived by art . . . . often as an imitation of something found in nature"; "feigned", fictitious", "assumed", "not genuine". Among the synonyms recorded by Webster are "unnatural", "spurious", and "counterfeit".

Dr. Heaton should recall the fate of "artificial silk", once erroneously applied to the regenerated cellulose fibres but long since replaced by the man-made word *rayon* by common consent.

Surprisingly, "artificial silk" is still to be found in British patent specifications, and even in the U.S.A. "Artificial Silk" Blacks and Blues are still offered for sale by certain dye firms.

William H. Cady

127 Power Street
Providence R.I.
U.S.A.

23rd August 1955

[1] Heaton, J. S., J.S.D.C., **71**, 403 (July 1955).

Thoughts on Labelling

In a store in Oxford Street, London, there was recently a display of lengths of soft furnishings. One length was labelled *Furnishing Fast and in Other Colours*. This is an ambiguous label, which leaves one in doubt as to whether the other colours were also fast. The 100% cotton and the cotton and rayon brocade lengths were also labelled fast, but none of the 100% rayon lengths were labelled fast: a good example of unintelligent labelling.

In the summer sales weeks another Oxford Street store had banner streamers of *Branded Goods Week* on all display windows. Actually, in one window only were there some examples of one branded line of ladies' outerwear. All the other windows were full of sales merchandise not displayed in the usual tasteful way found in London stores today. Surely, this was bad timing for emphasising branded goods. In February a Reuter message from Paris informed us that a man of twenty who bought a suit of wool cloth treated with silicones would still be able to wear it forty years later. It is to be hoped that the tailor would put in one of the pockets a packet of slimming tablets in case the wearer tended to put on weight. The technologist who claimed this had provided machinery which will subject wool, silk, and rayon materials to the equivalent of twenty to thirty years' ordinary wear in a few minutes. Doubtless he will also deal with the miracle fibres in the near future.

It is not unusual in stores which do a yardage trade to see materials displayed in length form with every cuttle mark showing and labelling it *crease-resistant*. Would such a display be condemned if the inaccuracy of informative labelling were made an indictable offence? Who would be responsible for the policing and on whose shoulders would the cost be placed? One of the admitted defects of the Utility scheme was that it was never adequately policed.

Has any estimate been produced of what compulsory informative labelling would entail to do the necessary policing? What size of technical staff and laboratories would be required? Who would lay down the tolerance figures? Who would pay?

At the 1954 Textile Institute Conference at Scarborough, mixture fabrics were labelled as to percentage content to the second place of decimals. Fabrics so labelled have also appeared in one display at Hamilton House. I have known many cloth designers, but I have never met one who calculated his blends to the second place of decimals. Surely, such labelling is a pedantic absurdity.

Will any responsible person maintain that any garment made from a natural, regenerated cellulosic, or so-called miracle fibre— even if given a stabilised finish— will not be improved by ironing after washing if the garment is to be worn as outerwear?

It is pleasing to note that one producer of one of the so-called miracle fibres is playing down the no-ironing stunt. In a recent exhibition catalogue an occasional ironing with a "rayon" setting is conceded.

Wringing is, however, banned; therefore the increasing number of housewives who possess a domestic washing machine fitted with a pair of wringing rollers will have to imitate Hamlet and recite on washing day—

To be wrung or not to be wrung, that is the question.

The "no-wringing" ban may account for the advice published in one paper to the men who wash their miracle fibre shirts in hotel bedrooms. When the washing is completed the saturated shirt has to be lifted out of the basin on a coat-hanger and allowed to drain over the bath ready for wear next morning. Unfortunately, there are many bedrooms in British hotels which have not a bath en suite. Personally, I have still to see a bath which has the necessary hook fitted on which to hang the saturated shirt conveniently.

It would be interesting to have a Gallup poll taken of the number of men who wash their shirts in hotel bedrooms. Would that common sense were on sale in the market places of textiles!

C. M. WHITTAKER

1 WEAPONNESS PARK
SCARBOROUGH

23rd August 1955

Notes

Meetings of Council and Committees
September

Council— 14th
Publications— 21st
Colour Index Editorial Panel— 6th and 21st
Perkin Executive— 23rd
Northern Ireland Symposium— 13th

Perkin Centenary Celebration 1956

In 1856, William Henry Perkin, then aged 18, discovered the first synthetic dye derived from coal-tar, later called *Mauve*, and from this discovery have developed the modern dyestuffs industry and the greater part of the world's organic chemical industries.

Thus, the basic discovery made by this young Englishman 100 years ago inspired the present-day pharmaceutical industry, synthetic fibres and plastics, pigments and resins for the paint trade, and other industries well recognised today as essential to modern life.

It is planned to celebrate in appropriate fashion, in London in May 1956, the centenary of Perkin's

discovery. Already extensive and influential support has been promised. The Patron will be H.R.H. The Duke of Edinburgh, K.G., K.T.

As the body which is probably most closely linked with the industrial application of the direct outcome of Perkin's work, the Society of Dyers and Colourists decided some time ago to inaugurate plans for the appropriate celebration in 1956 of the centenary of Perkin's discovery.

Other learned and scientific bodies have now joined the Society, and fully detailed plans are being prepared under the aegis of the following sponsoring bodies—

The Royal Society
The Chemical Society
The Society of Chemical Industry
The Society of Dyers and Colourists
The Royal Institute of Chemistry
The Association of British Chemical Manufacturers

Under the Patronage of H.R.H. The Duke of Edinburgh, the President of the Celebration is the President of the Royal Society, with the Presidents of the Sponsoring Societies as Vice-presidents.

An influential Organising Committee has been set up under the Chairmanship of Sir Robert Robinson, O.M., F.R.S. Subcommittees have been set up to deal with individual aspects of the Celebration, viz.—

Technical and Scientific Committee
Social Committee
Finance Committee
Publicity Committee

Whilst detailed plans are not yet completely formulated, the important question of finance has been fully considered, and an appeal for support for a £100,000 Fund has been issued over the signature of the Chairman of the Perkin Centenary Committee.

It is intended that the monies received shall be used mainly to set up a Trust Fund which will finance "Perkin Centenary Scholarships", intended to promote, advance, and encourage technical education in relation to all aspects of the fabrication and application of colouring matters.

The main Centenary Celebration will be held in London during early May 1956 and will take the form of a series of five Lectures dealing with the effects of Perkin's discovery on life and industry during the past 100 years. There will also be a Conversazione, at which an opportunity will be given for overseas delegates to the Celebration to meet one another and the delegates from Britain. A Banquet is to be planned at which, it is hoped, H.R.H. The Duke of Edinburgh will be present.

It is possible that a Memorial Volume will be produced to provide a lasting record of these Celebrations, which are designed primarily to honour the outstanding contribution of Perkin to the world's science and industry.

Manchester College of Science and Technology

A royal charter has been granted for the incorporation of a new, independent college with the above title. In due course the new body will enter into negotiations with the Corporation of Manchester for the taking over of the present Municipal College of Technology. The Society is entitled to nominate one representative on the court of governors.

The Clothworkers' Company

Mr. Owen Astley Bloxam has been elected Master of the Company for the year ending 31st July 1956.

Production of Dyes in the U.S.A. in 1954

Preliminary estimates of the U.S. Tariff Commission put the total production of dyes at 143 million lb., compared with 166 and 145 million lb. in 1953 and 1952 respectively.

Sales of dyes in 1954 amounted to 137 million lb. worth $160 million compared with 152 million lb. worth $168 million in 1953.

Production of Sulphur Black in 1954 was 11·5 million lb. (9·3 million lb. in 1953), of anthraquinone vat blue GCD 2·6 million lb. (2·5 and 1·8 million lb. in 1953 and 1952 respectively), of synthetic indigo 11·1 million lb. in 1954 (17·9 in 1953), and of Direct Black EW 5·6 million lb. in 1954 (6·3 in 1953).

37% of the production consisted of azo dyes, 22% anthraquinone vat dyes, 16% sulphur dyes, and 10% indigoid and thioindigoid dyes, there being a decrease in production of 8%, 19%, and 35% for azo, anthraquinone vat, and indigoid and thioindigoid dyes respectively, and an increase of 0·5% in the case of sulphur dyes. C. O. C.

New Books and Publications

The Chemistry of Synthetic Dyes and Pigments

Edited by H. A. Lubs. Pp. xiv + 734. American Chemical Society Monograph No. 127. New York: Reinhold Publishing Corpn. 1955. Price, $18.50 or £7 8s. 0d.

So wide is the range of this latest book on dye chemistry that it almost belies the appellation "monograph", which the *Oxford English Dictionary* defines as a "treatise on a single limited subject". Dr. Lubs has brought together the work of nineteen contributors, each a specialist in the field about which he writes, and all one-time staff members of du Pont's Jackson Laboratory. Like the two volumes of similar title by Professor Venkataraman which appeared a short time ago, this book, as its editor acknowledges, has drawn freely on the BIOS and FIAT reports, and in so doing has provided an admirable guide to the valuable information on dye and pigment manufacture which is scattered among them.

The book is divided into fourteen chapters. The first, *Benzene Intermediates* by A. C. Stevenson, after a brief summary of the electronic theory of substitution in the benzene nucleus, deals in turn with sulphonation, nitration, halogenation, alkylation, introduction of carboxyl and formyl groups, hydroxylation, and amination, as these reactions are used in the preparation of benzenoid dye intermediates. Included, too, are two sections headed "Oxidation" and "Reduction" and one covering heterocyclic compounds, e.g. carbazoles, pyrazoles, and quinolines. Worthy of note in this chapter is the part devoted to intermediates containing fluorine, which have aroused considerable interest in recent years.

Chapter 2, *Naphthalene Intermediates* by H. M. Pramelee, describes most of the important derivatives used in the dye industry and summarises in a discussion of the nitration of naphthalene and its sulphonic acids the series of papers by Hodgson and his co-workers which appeared in this *Journal* between the years 1943 and 1947.

Chapter 3, *Azo Dyes*, opens with a review of the theoretical aspects of the diazotisation and coupling reactions by S. N. Boyd, and goes on to deal with this large and important group of dyes by dyeing class. This approach provides for the practising dye chemist a more readable and interesting survey— or so your reviewer found— than the division on strictly chemical grounds into monoazo, disazo, etc. H. E. Woodward writes on both "Azo Dyes for Cotton" and "Azo Dyes for Wool", and in both sections gives a good account of developments which led from the early types to most of the important ones in current use. The tables reproduced (pp. 141 and 165) from the U.S. Tariff Commission Report showing the dyes produced in the largest amounts in the U.S.A. are of interest, and the author has borne these well in mind when choosing examples to illustrate the text. The absence of any reference to the modern neutral-dyeing metal-complex wool dyes (Cibalan type) is surprising. The disperse azo dyes are given separate treatment by J. F. Laucius, who does not mention two interesting features of this class of dye, viz. (*a*) the phenomenon of phototropism observed with some of the yellows and oranges that were used at first, and (*b*) the change of colour with heat that can be some slight inconvenience to the dyer. Another omission is any reference to the paper (Dickey *et al.*, *Ind. Eng. Chem.*, **45**, 1730 (1953)) by a group of Eastman Kodak chemists who report recent developments in fluorine-containing disperse azo dyes. The chapter closes with a short but useful summary of azo dyes soluble in organic solvents.

Azoic dyes are the subject of a separate chapter contributed by C. W. Maynard. It consists largely of a series of useful tables showing names, constitutions, special properties, and uses of coupling components, bases, stable salts, Rapid Fast Colours, Rapidogens, and Neocotones respectively.

Chapter 5 deals with *Miscellaneous Dyes* (S. E. Krahler) and Chapter 6 with *Sulphur Dyes* (N. M. Bigelow and O. Stallmann). The first of these includes all those dyes not belonging to the azo, anthraquinone, indigoid, sulphur, or phthalocyanine classes. In describing picric acid as the oldest artificial dye, the author mildly disagrees with the editor, who in the preface refers to Perkin's Mauve as "the first man-made dye". The reviewer found the placing of the references at the end of each section of "Miscellaneous Dyes", instead of at the end of the whole chapter as earlier in the book, to be a little confusing.

Anthraquinone Dyes and Intermediates forms easily the longest chapter, being allotted a considerably greater proportion of the book than Venkataraman gives this group in his two volumes. It is split into five parts—"Intermediates" by F. B. Stilmar and M. A. Perkins; "Acid Dyes" and "Metallisable Dyes", both by E. C. Buxbaum; "Disperse Dyes" by C. F. Belcher; and "Vat Dyes" by a group of contributors. The first part provides a well referenced account of the various methods of synthesising the anthraquinone ring and of the preparation of all its more important simpler derivatives. One small omission is the names by which certain hydroxyanthraquinones are known. 1:4-Dihydroxyanthraquinone is correctly given on p. 368 as quinizarin, while others, e.g. anthrarufin, go unnamed, though the names appear in the index, which refers the reader to the appropriate page. In the several methods given on p. 414 for preparing "bromamine acid" the sulphonation of 1-aminoanthraquinone with chlorosulphonic acid described in FIAT 1313 (Volume II) is, surprisingly, not included.

The section on disperse dyes lists most of the important anthraquinone derivatives used in this way. In contrast to the manner in which other parts of the book select commercial types when choosing examples, this section quotes many,

particularly in Tables 1 and 2, that are not so used. A mistake which has already appeared several times in print is repeated once again (p. 423): Celliton Orange R is stated to be 1-methylaminoanthraquinone instead of, as it should read, 1-amino-2-methylanthraquinone. No reference is made to the intensive work, described in the patent literature of the past few years, in search of blues fast to burnt gas fumes and light, which has resulted in the marketing by at least one American firm of dyemakers of an anthraquinone dye having these properties; nor to the related subject of gas-fume fading inhibitors.

The long section (120 pp.) on vat dyes works systematically through this field of complex chemical compounds. First come the carbocyclics in order of increasing complexity from the benzoquinones and acylaminoanthraquinones to the dibenzanthrones. Then follow those based on a five-membered heterocyclic system—the carbazoles, anthrapyrazolones, oxazoles, thiazoles, and iminazoles—and finally the six-membered heterocyclics, which include the pyridones, acridones, and azines. The chapter is completed with a section on solubilised types, and a miscellaneous collection which refers among others to the recently introduced phthalocyanine vat dye.

The next chapter, by A. J. Johnson, provides a concise and readable account of the *Indigoid Dyes*. It is followed by *Phthalocyanine Pigments* by N. M. Bigelow and M. A. Perkins and *Phthalocyanine Dyes* by W. S. Struve. In keeping with the opinion expressed in the preface that "the discovery and development of the phthalocyanine pigments is perhaps the greatest advance in the dye field during the past generation" the treatment of this group of colouring matters is considerably more extensive and detailed than in earlier books on dye chemistry. Worthy of note in the first of these two chapters are a useful account of the various ways in which phthalocyanines are made suitable for use as pigments and a summary in tabular form of the preparation and properties of a number of less familiar phthalocyanines. The chapter on dyes recounts the ingenious devices by which chemists have sought to take advantage of the remarkable properties of the phthalocyanine structure in the colouring of textiles, oils, and lacquers. It mentions the interesting synthesis *in situ* from 1:3-di-imino*iso*indoline, though the author could have gone on to associate this discovery with Phthalogen Brilliant Blue F3G (Gund, F., J.S.D.C., **69**, 671 (1953)).

The chapter which follows, *Organic Pigments* by E. R. Allen, discusses first the physical properties, use, and structure of this group of colouring matters, and then proceeds to deal with them in chemical classes, beginning with those compounds—nitro, azo, and certain anthraquinones and indigoid derivatives—which require no further chemical processing, and following with those which do. The latter are split into cationic derivatives, e.g. Methyl Violet B precipitated with phosphomolybdic acid or other agent, and anionic derivatives, which are converted into their metallic compounds to produce e.g. the Lithols.

Chapter 12, by Donald Graham, offers a digest of modern theories of colour and constitution.

The remainder of the book is taken up with—(*a*) a list of common names used in the industry and the substances to which they refer; (*b*) a very useful and complete bibliography, in which the only omission noted in a cursory examination was mention of the "Dyestuffs and Intermediates" chapter of the Society of Chemical Industry's *Reports on the Progress of Applied Chemistry;* and (*c*) an index of dye names and a subject index, which is not quite so thorough as one has come to expect of American publications. Thus every mention of a subject is not referred to; e.g. "quinizarin" was seen on four pages which go unnoticed in the index, and an entry referring the enquirer to the much publicised topic of fastness to burnt gas fumes (p. 421) would not have been out of place. No author index is provided.

Summing up, your reviewer was impressed by the following features—(i) the way in which so much information has been compressed into so compact a volume, thus making it especially valuable to advanced students and practising chemists; (ii) the orderliness of presentation; (iii) the easy-to-read style—so frequently lost in writings of this sort—for which one can forgive the occasional lapsing into "semi-commercialese", such as on p. 407, where one reads: "This color also has a favorable economic picture although light fastness is not so good . . . "; (iv) the free use of very clear, neat, and uniform formulae; (v) the clarity of the type and headings used; and (vi) the habitual quoting of *Colour Index* and AATCC "Prototype" numbers. Two minor criticisms are—(1) the omission of the patentee's name from all the non-American patent references and (2) a general lack of comment on recent (say up to the end of 1953) trends and developments, which ought, perhaps, to be possible where the effort, as in this case, is divided among a number of contributors.

All those whose interests and work are concerned with dyes and pigments should have this book at least within consulting distance. While it covers almost the same ground as Venkataraman's book, though without the same detail, it has something not possessed by the earlier publication, particularly in its approach to the subject, that will make it useful especially to the practical dye chemist.

It may not reach, as the dust cover proclaims—"the *ultimate* in dye chemistry"—whatever that is—yet Dr. Lubs and his team of contributors are to be congratulated on the truly worth-while result of their efforts. R. K. Fourness

La Couleur dans les Activités Humaines

By M. Déribéré. Pp. viii + 242 + 51 Fig. + 5 colour plates. Paris: Dunod. 1955. Price, 1980 francs.

Lightness, gaiety, and colour characterise much of the modern forms of architecture and other decorative arts, both in domestic and in public buildings. This is apparently a result of Continental, and particularly Scandinavian, influences,

stimulated greatly in this country by the admirable displays of the 1951 Festival of Britain, especially the South Bank exhibition. In addition to the use of colour in this way for its aesthetic appeal, it is being increasingly used in industry for utilitarian purposes: in factories the wide use of colour-painting schemes not only serves to relieve the appearance of drab surroundings, but also acts as a positive aid to safety and increased production by facilitating the identification of machinery and of service supplies. This is a practice which was in use even before the 1939–1945 war, but its use was extended by the requirements of the intensified industrial production of the war years: safety was improved and it acted as a psychological antidote to the black-out.

It is essential for the colour schemes used in these new ways to be carefully planned if they are to be both pleasing to the eye and effective in their practical aims. This book, written by the head of the lighting bureau of the French Mazda lamp company, is designed to give an informal account of the principles of colour and of its practical use in the decoration of home, office, school, shop, and factory. It includes a succinct account of the physical basis of colour vision, colour specification systems, and colour measurement by the tri-chromatic system, and is well illustrated with line diagrams and reproductions in colour and mono-chrome. This is followed by a description of the relationship between the visual appearance of coloured objects and the nature of the illumination, with some account of the psychological and physiological effects of colour and the influence of illumination of different colours upon plant and animal life. The use of colour in decorative schemes for houses and industrial buildings is illustrated by the colour plates.

This is a compact and useful manual of information, valuable for all who may be interested in the physical aspects of colour, including students studying for Section B of the examination for the Associateship of this Society.

The printing, paper, and binding are of high quality. C. H. GILES

Basic Chemistry of Textile Preparation

By S. R. Cockett and K. A. Hilton. Pp. vii + 197. London: National Trade Press Ltd. 1955. Price, 21s. 0d.

The declared object of this book and its companion volume, *Basic Chemistry of Textile Colouring and Finishing*, which has still to be published, is to provide a complete theoretical course in basic textile chemistry for students and for workers already in the industry. The first four chapters, which amount to well over one-third of the book, are thus concerned with the structure and properties of the natural fibres, plastics, and manufactured fibres, in that order. The method of treatment and the clarity of the presentation make this by far the most valuable part of the book. The essentials of fibre structure and the relation between structure and chemical and physical properties are clearly brought out, and the inclusion of the section on plastics, in which brief reference is made also to drying oils, silicones, and natural and synthetic rubbers, serves to remind the student that all are high polymers with many common characteristics. Full use has been made of chemical formulae, equations, and diagrams. Chapter V gives details of the main properties of the various groups of fibres. Data for each type are presented in tabular form, but the method of presentation does not readily permit comparison of fibre with fibre. In a textbook this is, perhaps, unfortunate, for students should be encouraged to relate observed differences in properties with known differences in physical and chemical characteristics.

The second section, which anyone buying the book on its title would expect to be at least as detailed as the first, is much less satisfactory. Bleaching, in particular, is rather summarily dealt with, and while a good deal of information is given on the chemistry and the properties of the products used in the various processes, there is a general tendency to concentrate on these and to say too little about the fundamentals of the process itself. Under the heading "subsidiary processes" some account is given of mercerising, carbonising, and milling, and there is a very brief reference to chlorination. The latter contains the unsatisfactory, incomplete statement that "chlorinated wool dyes to a heavier shade with most dyestuffs". The description of milling is similarly prefaced by a very incomplete account of the felting of wool. A short description of colour, its origin and measurement, and the functioning and defects of the human eye has been added to the section on bleaching, and the book is completed by a chapter briefly describing some related industries, including papermaking, laundering, dry cleaning, and leather manufacture, and a final one on textile testing and defects. The purpose of the descriptions of the related industries is to enable analogies to be drawn between the textile industry and others using fibrous materials. This end would have been better served if less detail had been included and more emphasis placed on features and problems common to both. Some of the statements regarding laundry practice, although possibly true in rare, specific instances, may convey wrong impressions. Thus sequestering agents are not generally used to prevent lime soap formation, but hard water is softened before use; the temperature of the last wash in a white work process should be as near 212°F. as possible; when using a relatively high-titre soap, the first two rinses should be really hot.

If it was absolutely necessary that the course be spread over two volumes, it might have been better if the first had concluded with a comparative treatment of fibre properties, leaving all textile processing to be dealt with in the second. No completely satisfactory division of textile processing into preparation, colouring, and finishing is possible and, even if it were, such an approach would not be the most suitable for students, who need above all to be reminded of the inter-dependence of all processes. Some who purchase this book on a strict interpretation of its title may perhaps justly complain that it does not live up

to it, as the space devoted to textile preparation is only one-sixth of the total. They will probably not be appeased by the quality and the usefulness of the first half, which will be a pity.

C. B. STEVENS

Practical Textile Chemistry
With Special Reference to the Structure, Properties and Processing of Wool

By J. W. Bell. Pp. xvi + 259. London: National Trade Press Ltd. 1955. Price, 30s. 0d.

In the foreword to this excellent book, Professor J. B. Speakman states: ". . . a craft industry has been transformed into an applied science . . . but textbooks dealing with the practical training of the textile technologist are still lacking." It is therefore very fitting that the University of Leeds should produce the first mature, authoritative work dealing with Practical Textile Chemistry.

The book deals primarily with wool, other fibres being only briefly discussed as necessary in the final chapter, concerned with identification and analysis of fibre mixtures.

Dr. Bell presents a most comprehensive scheme of practical work on the chemistry of wool. Intended for use in the training of the student, it will be found a useful work of reference to all practising textile technologists, but must be judged as a teaching manual. In this respect it is first-rate. The development of the work stems from the structure, properties, and reactions of wool, with a sequence of experiments demonstrating almost all known features of the morphology, constitution, and reactions of the wool-fibre. This section is followed by one dealing with the materials used in the processing of wool, and another section covering the standard processes themselves, such as scouring, crabbing, carbonising, milling, bleaching, and shrinkproofing. (In neither of these sections is any experiment included concerned with mothproofing agents or the mothproofing process.) The final section treats in a suitably introductory fashion the identification and quantitative analysis of fibre mixtures, with a useful appendix of essential facts.

The detail given for each experiment is such as to be suitable for use by students. In many experiments references are given to original papers covering the topic more fully, but the method given in the book is not necessarily identical with that in the original paper. Deliberately, no indication is given of the comparative efficiency, accuracy, or convenience of the several methods described for a similar purpose, since the student should be trained to develop a critical approach to all problems. As an example of this, one finds (pp. 184–187) descriptions of three different methods for the determination of acid in wool. (A better reference than those given for this determination might be *Analyst*, **63**, 782 (1938).)

The book is clearly illustrated by diagrams of apparatus assemblies, it is well documented and well indexed, and the accounts are easily followed.

Owing to the concentration on wool, there is no experiment using the viscometric method for assessment of fibre-damage. Were the book to be extended in a second edition to cover wool and allied fibres, the introduction of an experiment on the fluidity method for silk-damage determination would introduce the student to a method applied extensively in the cellulosic and man-made fibre fields. At the same time, it could be suggested that the tests for metals in wool could be extended to include quantitative estimations of copper, iron, chromium, and possibly other metals.

With such an excellent lead, it is to be hoped that a companion volume of similar calibre dealing with cellulosic and allied fibres may soon be forthcoming from an appropriate source.

R. L. ELLIOTT

Chemie und Physikalische Chemie der Textilhilfsmittel
Band I

By Herbert Frotscher. Pp. 188. Berlin: VEB Verlag Technik. 1954. Price, DM 17·00.

According to the preface, the author was asked by the publishers to write a concise account of textile auxiliaries, which would give young textile chemists as well as practical finishers a deeper insight into the relation between chemical structure and the properties of textile auxiliaries. It is therefore a textbook, but one which assumes an accurate knowledge of textile processes and a good knowledge of chemistry and physics. It starts with a brief account of the chemical and physical properties of fibres with special reference to their chemical constitution. Then follows an account of their behaviour in aqueous solutions used in textile processing.

The heart of the book, however, is devoted to the chemistry and physics of surface-active substances. Here, again, the leitmotiv is the relation between molecular constitution and wetting and scouring properties. It is very theoretical, and rightly so, for, although theories by their very nature must be controversial, it is only by the study of theories that one gains a deeper insight into phenomena, even the phenomena of textile processing. This section naturally concludes with a valuable systematic classification of surface-active agents according to their chemical constitution.

The use of these auxiliaries is then discussed in separate chapters dealing with dyeing, printing, washing, scouring and milling, kiering and bleaching, mercerising, and carbonising. Their use in finishing processes generally is left for treatment in Volume 2.

There is a good list of the literature referred to in the text, and the index is followed by an up-to-date list of the commercially known textile auxiliaries under their trade names.

It is a book which should be in every textile works library or laboratory. R. GAUNT

Principles of Polymer Chemistry

By P. J. Flory. Pp. xvi + 672. Ithaca N.Y.: Cornell University Press (London: Oxford University Press) 1953. Price, 68s. 0d.

The very rapid growth of polymer science during the past twenty years has been, in no small measure, stimulated by the work of Professor Flory, who has made fundamental contributions to the understanding of polymerisation, polymer crystallisation, rubber elasticity, the equilibrium properties of polymer solutions, and many other aspects of polymer science. In this book he presents an account of the physicochemical principles upon which modern polymer chemistry is based.

Following two introductory chapters, in which a very readable account of the historical development of polymer chemistry is given and the types of high polymers are clearly defined and classified, three chapters are concerned with the mechanisms and kinetics of polymerisation. Condensation, free-radical polymerisation, and copolymerisation are discussed in some detail, and ionic polymerisation is treated briefly. The structure of both linear and cross-linked polymers is then considered, and also the determination and distribution of molecular weights. A chapter on chain configuration and the random-flight approximation is followed by a discussion of the elasticity of rubber. The remainder of the book is concerned with polymer–liquid interaction. The limitations of the elementary lattice theory treatment of the thermodynamics of polymer–liquid systems are shown, and thermodynamic properties are derived statistically by Flory's own methods. The use of these is illustrated by application to examples. The methods and results are then applied to problems of solubility, phase separation, and swelling. The final chapter is concerned with the viscosities of dilute solutions of high polymers in terms of the theories developed by Flory and his co-workers.

Throughout the book the viewpoint adopted is generally that of the author and his school, and there are many references to their work. Emphasis is on fundamental principles, which are clearly explained, and while experimental methods are outlined and ample references given, detailed results are not generally included. Some knowledge of statistical thermodynamics is required in certain sections of the book. Inevitably, in a book of this type, some topics must be considered only briefly or omitted. Thus, dynamic behaviour is not included, and there is little consideration of fibre-forming polymers as such. There is some discussion of polymer crystallisation, but cellulose, its derivatives, and polypeptides are only briefly considered. The field covered, however, is a very wide one, and the book will be invaluable, not only as a reference book and textbook, but also as a source of inspiration and stimulus for all research workers in the field of polymer science.

W. R. Moore

A Systematic Handbook of Volumetric Analysis or the Quantitative Determination of Chemical Substances by Measure, applied to Liquids, Solids, and Gases

By Francis Sutton. 13th edition 1955, revised by Julius Grant. Pp. xiv + 752. London: Butterworths Scientific Publications. Price, 63s. 0d.

It is certain that no living chemist can remember the time when there was no "Sutton", and those who owe at least part of their basic training to it must be in a healthy majority. All considered, it is surprising that the time-lag between the twelfth and thirteenth editions should (even after subtraction of the war years) be the longest of all. Our old friend has benefited considerably from the face-lift, and is now an even better proposition than before.

The general plan of the book is unchanged—a sure sign that it has proved satisfactory over the years—and the actual substances whose analysis is covered are much the same as before. The differences fall under three headings—(1) The overall balance of the book is altered, and of the 120 pages added, 56 are within the statement of general principles; this section is thereby virtually trebled in length. This can serve only to enhance the value of the book to the student, for whom it provides a clear and useful summary. The speed and mode of progress through the fundamentals indicate that the book is intended as a refresher for those whose graduate days are many, or for use in conjunction with a course of study. (2) New analytical procedures are included; standard methods, where they exist, are given preference, and methods of lesser importance are indicated rather than detailed. Particularly welcome is the inclusion of references to polarographic and high-frequency methods, and textile chemists are likely to welcome the extensive table of fluorescent pH indicators—which can be used in dark-coloured solutions such as spent kier liquors. (3) The typography is greatly improved, the paper is of good quality, and the English is freed from a number of rather dated redundancies. The practice of foot-notation (which is always liable to run riot) is abandoned, and the numerous literature references are collated at the end of each section. The binding alone is inferior to the rest of the book, and is hardly of three-guinea standard.

This book will doubtless be reviewed, in later editions, by our great-grandchildren, but the present rate of development of analytical resource makes it unlikely that twenty years can ever be allowed to elapse between any other two successive editions.

J. W. Duarte

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes.
Any publication abstracted may be referred to by members of the Society on application to
Dr. C. B. Stevens, Dyeing Department, Leeds University

Badische Anilin- und Soda-Fabrik

PALATINE FAST DYES ON WOOL— This loose-leaf-style card (German text) contains dyeings in three depths on wool cloth of 39 Palatine Fast dyes and no less than 105 mixture dyeings covering a wide range of colours, particularly fawns, greys, drabs, dark browns, greens, blues, and navies, for the production of which these strongly acid-dyeing premetallised dyes are particularly suitable.

FASHION COLOURS ON PERLON HOSIERY— This card contains dyeings on woven Perlon material of a range of 13 Perliton dyes and 63 dyeings on knitted Perlon stocking material. The latter cover a wide range of the colours used on ladies' hose.

The Clayton Dyestuffs Co. Ltd.

CHLORANTINE FAST DYES ON COTTON AND VISCOSE RAYON YARN— This card contains dyeings in three depths on cotton and viscose rayon yarn of 64 Chlorantine Fast direct dyes, including 43 of the "LL" type distinguished by their excellent fastness to light. The dyeing characteristics of each dye are represented graphically, and the text includes information on their behaviour at 120°c. under neutral conditions in presence and absence of ammonium sulphate and under alkaline conditions in presence and absence of Synchromate Mordant. Ammonium sulphate has been found to be effective in preventing dye decomposition when using Glauber's salt alone, while Synchromate Mordant is recommended when soda ash is present in the dyebath.

DYES FOR HOSIERY YARN— This card contains dyeings on wool yarn of 38 dyes including acid (Benzyl and Benzyl Fast), chrome, and neutral-dyeing premetallised (Cibalan) types. They have been chosen for their level-dyeing properties and their ability to give dyeings of adequate fastness to light and wet treatments on hosiery yarns. Fastness to light, perspiration, and washing has been assessed according to the procedures recommended by the Society, and, in addition, an assessment is given of the behaviour of dyeings when subjected to non-shrink treatments using testing conditions corresponding to those obtaining in the Dylan, Epilox, Lanfix, Melafix, Negafel, papain, and Woolindras processes.

CHLORANTINE FAST BLUE 9GL— This direct dye gives dull greenish blues of good fastness to light on cellulosic fibres. The fastness to water and perspiration is improved by aftertreating with Lyofix EW, but the hue is reddened and the light fastness impaired. It is not recommended for dyeing materials subsequently to be crease-resisted, but can be used on goods to be vulcanised. Dyeings may be discharged to white under neutral and alkaline conditions. Fastness figures on cotton include— Light 6, washing 3, perspiration 4.

NAPHTHOCHROME VIOLET RB: SYNCHROMATE VIOLET RB— These designations describe a chrome dye suitable for dyeing afterchrome, on-chrome, and by single-bath methods to give bright violets on loose wool and slubbing. It is particularly recommended as a component for navies. It is also suitable for dyeing polyamide fibres, provided that care is taken to ensure that chroming is complete. Fastness figures of a dyeing by the Synchromate method include— Light 4, alkaline milling 5, potting 4–5.

The Geigy Co. Ltd.

IRGALITE AND IRGACHROME COLOURS FOR P.V.C. PLASTICS — This card contains colourings on polyvinyl chloride film of a range of 20 Irgalite and 6 Irgachrome pigments, the former being shown on both transparent and opaque material, the latter on transparent material only. The colourings obtained with these special ranges of organic pigments are not subject to colour migration and chalking and have excellent stability to heat, and their light fastness satisfies the most stringent requirements. The relevant fastness data are appended below each sample, and the text includes full details of the assessment of the fastness properties.

DYESTUFFS FOR SILK— This card contains dyeings on unweighted silk cloth of 168 dyes classified as follows— ordinary acid dyes 46, Polar and Neutral dyes 26, Irgalan 18 and Irganol S 4 dyes, Diphenyl and Diphenyl Fast dyes 32, Solophenyl dyes 34, and basic dyes 8.

TINOPAL WG— A fluorescent bluing agent for wool, silk, and animal fibres generally.

TINEGAL W— This is a non-ionic auxiliary product having an affinity for dyes of many types. Among its many uses, it is recommended as a levelling and stripping agent in wool and polyamide fibre dyeing and for direct, vat, and azoic dyeings; and for promoting the level dyeing of "tippy" wool and faded garments. It may be selective in its action under certain conditions, and its action is greatly inhibited by anionic finishing agents.

Imperial Chemical Industries Ltd.

BRENTACET DYESTUFFS FOR ACETATE RAYON AND NYLON— These are presumably mixtures of selected coupling components and diazotisable bases, since they are applied to the fibre from aqueous suspension using a modified azoic technique, the colour being developed by treating the "dyed" material in sodium nitrite and hydrochloric or formic acid. The suspension is prepared using soap flakes and soda ash plus caustic soda where permissible; Dispersol VL and common salt are added to the dyebath. Five members of the range are described— Scarlet G, Red B, Bordeaux B, and Black B, which may be dyed on acetate rayon and nylon; and Blue B, which is recommended only for use on acetate rayon. Dyeings on both fibres are characterised by brightness of hue, high wet fastness, and high resistance to chlorinated water. Fastness to light on acetate rayon is good, but somewhat lower on nylon. These dyes (except Blue B) may be used in mixtures; they are not suitable for printing. Fastness figures for Brentacet Red B include— *On Acetate Rayon:* Light 6, hot pressing (wet) 5, washing at 55°c. 4–5. *On Nylon:* Light 3, hot pressing (wet) 5, washing at 55°c. 4–5.

DISPERSOL FAST YELLOW GR— This disperse dye gives bright reddish yellows of very good fastness to light on acetate rayon, nylon, and Terylene. On acetate rayon and nylon its temperature-range properties and rate of exhaustion make it very suitable for dyeing on the jigger and winch, but its build-up on nylon is lower than on acetate rayon. It has good build-up properties on Terylene, particularly when dyed above 100°c., and in medium depths it is stable to a heat-treatment for 15 sec. at 170°c. In combination with Duranol Red 2B or X3B and Duranol Blue G it is of value for dyeing Terylene–wool mixtures. Fastness figures include— *Acetate Rayon:* Light (pigment-delustred) 6–7, sublimation 4–5, washing (Test No. 1, once at 40°c.) 4. *Nylon:* Light 5–6, sublimation 3, washing (Test No. 1, once at 40°c.) 3–4.

ALCIAN DYESTUFFS PRINTED ON COTTON PIECE GOODS— This card contains twelve prints cut from full-scale productions and illustrates the more important applications of the four members of the Alcian X range— Yellow GX, Greens 2GX and 3BX, and Blue 8GX. These include roller prints of Alcian dyes alone and in conjunction with Soledons on Brenthol AS prepare, of Alcians alongside Soledons and Brentogens and also alongside vat dyes; and screen prints of Alcian dyes alongside Soledons. Full production details are given for five of the patterns. The remainder were produced by commission printers; the dyes used are given together with brief comments on the procedure adopted in each case.

SELECTED DYESTUFFS PRINTED ON WOOL AND NATURAL SILK— This particularly massive pattern card contains 191 direct prints, 96 on chlorinated wool delaine and 95 on unweighted silk crêpe. The primary considerations governing dye selection have been solubility and ease of fixation in conjunction with colour and fastness properties. Acid dyes from the Carbolan, Coomassie, Disulphine, Lissamine, Naphthalene, Solway, and Ultralan ranges and

direct dyes from the Chlorazol and Durazol ranges have been selected to give the printer the widest possible choice. The text includes details for preparing the cloth for printing and six printing recipes; full fastness data are presented in tables, and the relevant figures for fastness to light, washing, water, sea-water, and perspiration are appended alongside each pattern together with a reference to the printing process employed.

DIRECT AND DISPERSE DYESTUFFS ON NYLON–CELLULOSIC UNIONS— This booklet describes the application of direct dyes to cellulosic fibre–nylon mixtures to produce either solid dyeings, using disperse dyes in the same dyebath to dye the nylon component as required, or dyeings in which the nylon is reserved. The uptake of direct dyes by nylon is reduced under alkaline dyebath conditions, and addition of up to 2% of soda ash calculated on the dry weight of the material gives good reservation of the nylon when using small amounts of dye. The risk of partial or complete destruction of alkali-sensitive dyes above 90°C., particularly when viscose rayon is present, should be remembered, and also the possibility of unlevel dyeings resulting from the salting-on effect of the soda ash. Where reservation is desired using high percentages of dye, addition of 6% of Taninol WR is preferred to soda ash, since it is more effective and does not produce conditions under which dye breakdown occurs or exert any salting-on effect. It does, however, darken on exposure to light, so that the amount used should not exceed 6%, and cause some reduction in light fastness on the nylon component. Twelve dyeings on an 85 : 15 viscose rayon–nylon staple blended mixture cloth are included.

TECHNICAL INFORMATION LEAFLETS— *Dyehouse No. 255. The Dyeing of "Terylene" Polyester Fibre: Supplement No. 4*— Light (daylight and Fade-Ometer) fastness figures are given for dyeings of 13 disperse dyes applied without a carrier and in presence of Tumescals PH, OP, and D respectively. The results indicate that, in general, Tumescal PH exerts a more marked adverse effect than the others, but of the dyes particularly recommended for dyeing Terylene only Duranol Red X3B is severely affected.

Dyehouse No. 256. Discoloration of Textiles by Shirlan— Shirlan Paste and Powder (essentially salicylanilide) and particularly Shirlan NA (the corresponding sodium salt) produce yellow or brown discoloration when the material to which they have been applied is exposed to light if traces of alkali or chlorine are also present.

Dyehouse No. 258. Cirrasol OD for the Softening of Paper.

Dyehouse No. 261. The Washing Fastness of Dyestuffs on Mordant Chrome Gloving Leather— A modified washing test is described based on the washing test for textiles recommended by the Society in the *Second Report of the Fastness Tests Committee* (2nd edition 1950, "Washing", p. 9). Fastness figures are given for those dyes which were rated 3 or better when dyeings were subjected to the recommended test.

SURFACE-ACTIVE AGENT LEAFLETS— *No. 9. Aphrosol FC (2nd edition)*— This is a foaming agent for the production of light-weight concrete and cement products.

No. 22. Vantoc AL— The properties and uses of this surface-active bactericide of the higher-alkyl-trimethylammonium bromide type are described in detail, and methods of determining its concentration in solution and assessing its bactericidal power are included.

No. 25. Lubrol G— This product is an emulsifying agent and detergent for incorporation in paraffinic oils to be used for degreasing metals and general cleaning.

AUXILIARY PRODUCTS PAMPHLETS— *No. 6. Astol A (3rd edition)*— An organic-solvent emulsion containing trichloroethylene for scouring and spotting.

No. 9. The Shirlan and Shirlan NA Brands of Antimildew Agents.

No. 32. Resist Salt L.

No. 49. Calatac VA (3rd edition)— A synthetic-resin finishing agent for textiles.

No. 60. Dipsanil V— A stabilised paraffin-wax emulsion containing hydrolysable aluminium salts for producing water-repellent finishes by a single-bath treatment.

No. 90. Quintolan W; Application to Textiles and Paper— Quintolan W is a solution in isopropyl alcohol of an organic chromium compound introduced for producing water-repellent finishes on textiles, particularly wool and synthetic fibres, and on paper.

No. 93. Bedafil CF— This is an aqueous anionic dispersion of an inert polymeric resin for filling light leather.

E.I. du Pont de Nemours & Co. Inc.

TECHNICAL BULLETIN, VOLUME 11, NO. 1— This issue includes notes on Capracyl dyes on nylon and descriptions of a number of new products. General articles include the dyeing and finishing of sweater bodies of high-bulk Orlon, the dyeing of nylon carpets, the printing of Orlon Type 42, and the continuous dyeing of loose wool in a scouring train. It also contains a nomenclature list of the various types of manufactured fibres currently in use, and conversion nomographs for yarn cross-sections and strength and modulus units.

LATYL BRILLIANT BLUE BG— This disperse dye gives bright blues, redder in hue than the 2G brand, on polyester fibres, and builds up better than the latter dye. The light fastness of dyeings depends upon the dyeing method employed, those produced above 100°C. or by the Thermosol process being much superior to those produced at 100°C. using *o*-phenylphenol as carrier. The light fastness of the latter is, however, greatly improved by heating the material at 150–195°C. for 1–4 min. after scouring and drying. It is very resistant to gas-fume fading. Fastness figures of a 2·0% dyeing on Dacron staple produced using *o*-phenylphenol as carrier include— Light (Fade-Ometer) control 4, sample heat-treated for 1 min. at 195°C. 7–8; washing (AATCC No. 2) 5–4 GW; sublimation (dry steam for 20 min.) 5.

LATYL BLUE 4R— This disperse dye gives reddish blues on polyester fibres which are bluer than those obtained with Violet BN. It is more economical than the latter for producing many mixture dyeings, including tans, browns, and greys. It is not recommended for navies. It may be dyed by conventional methods using carriers, above 100°C. under pressure, or by the Thermosol process. Acetate-rayon and nylon effects are only lightly dyed in the presence of a phenolic carrier. Fastness figures for a dyeing on Dacron staple produced using *o*-phenylphenol as carrier include— Light (Fade-Ometer) 3–4, washing (AATCC No. 3) 5, sublimation (dry steam for 20 min.) 5–4 D.

SEVRON ORANGE L; SEVRON RED L— These are basic dyes introduced for dyeing Orlon to give dyeings having very good fastness to light. They are recommended for use alone and in mixtures for browns and light and dark greys. If applied under distinctly acid conditions a more bathochromic colour is obtained and a dyebath pH of 5 is recommended. Dyeings of both dyes appear markedly yellower in artificial light, but if Sevron Blue B is also present, the shift of the latter to red assists in counteracting this effect. Orange L can usefully replace some of the Yellow R and Brilliant Red 4G to give deeper and more pleasing blacks. Fastness properties include— *Sevron Orange L:* Light (Fade-Ometer) 7, washing (AATCC No. 3) 5–4 R. *Sevron Red L:* Light (Fade-Ometer) 7, washing (AATCC No. 3) 5–4 BL.

Sandoz Products Ltd.

ALIZARINE LIGHT RED VIOLET 3RL: XYLENE FAST VIOLET P3R— This acid dye gives bright reddish violets on wool, silk, and polyamide fibres. It is dyed on wool from an acetic-acid bath, and its second designation as a Xylene Fast P dye indicates its suitability for use alone and in mixtures for dyeing yarn and cloth where levelness and good wet fastness are demanded. It is unaffected by chromate in the dyebath and is also of interest for dyeing the wool component of wool–cellulosic fibre mixtures. It builds up well on nylon to give dyeings of very good wet fastness. Fastness figures on wool include— Light 6, washing (40°C.) 4–5, sea water 5, alkaline milling (mild) 4.

CUPROFIX NAVY CLW: RESOFIX NAVY CLW: CUPROFIX PRINTING NAVY CLW— The multiplicity of designations under which this aftercopperable direct dye is marketed indicates its versatility. Thus it may be aftertreated with

copper sulphate, Cuprofix 8L, and Resofix CU to give navies of good fastness to light and washing on all types of cellulosic fibres. Dyeings have good stability to crease-resist finishing. It is also of interest for direct printing and can be discharged to white using the Cuprofix White discharge process. Fastness figures for a dyeing on cotton aftertreated with Resofix CU include—Light (daylight) 7, washing (95°c.) 4–5, perspiration 4.

DIRECT DYES SUITABLE FOR ANTI-CREASE WORK—This card contains dyeings of 51 direct dyes, a urea–formaldehyde crease-resisted dyeing being included in each case to indicate the effect of the treatment on hue. Because of the importance of the effect of this type of finish on the hue and fastness to light of dyeings, the dyes listed have been divided into two groups. The first contains those dyes giving dyeings which are unaffected in hue and which exhibit the highest light fastness obtainable in that particular colour. Group 2 contains those dyes which, while not quite up to the standard of those of Group 1, have been accepted as a result of comparatively long established usage.

ULTRA-DISPERSED SANDOTHRENE DYESTUFFS—This card describes a range of 14 vat dyes now available as both powders and pastes, the average particle size of which is 0·2–1μ. It is thus possible to obtain still finer dispersions than are afforded by the Extra Fine Powder and Paste Ultrafix brands, and the new range is particularly recommended for dyeing cloth by the pad–jig and pad–steam techniques and for package dyeing in circulating-liquor machines using the pigmentation method. The text includes details of application to yarn and cloth and the results of two tests designed to demonstrate the relation between particle size and penetrating power.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Mixing, Emulsifying etc. Machine. Lang–London–Limited. *BP* 733,693

Wet Processing of Freshly Spun Rayon Cakes. Skenandoa Rayon Corpn. *USP* 2,690,375

Treating Rayon Cake. Celanese Corpn. of America. *USP* 2,689,192

The cake is enclosed in a paper cover. This cover is protected during wet processing and drying by covering it with a textile fabric sock. C. O. C.

Thread-storing Thread-advancing Reel. American Viscose Corpn. *USP* 2,690,405

Continuous Treatment of Freshly-formed Filaments. Courtaulds. *BP* 734,150

Thread-storing Thread-advancing Reel in which Freshly-formed Filaments can be treated with Hot Liquids. Courtaulds. *BP* 734,234

Setting Thermoplastic Fibres. R. C. Parkes. *USP* 2,691,202

A machine in which the fabric passes under controlled tension over heated rollers. C. O. C.

Highly Lustrous Mercerised Cotton Thread. W. F. Luther. *USP* 2,686,955

A mercerising machine for producing highly lustrous cotton yarns, free from fuzziness and very level dyeing. C. O. C.

Adjusting the Nip between Rollers. Andrew Johnson & Son. *BP* 733,277

Ultra-rapid Wet Processing of Yarn, Cloth, etc. in Rope Form. Mezzera. *BP* 734,044

A winch machine in which the winch has a circular cross-section and has on its surface ribs extending in the direction of its axis. The height and angular spacing of these ribs are such that a plane extending through the edges of two adjacent ribs intersects the surface of the winch between them. C. O. C.

Stenter. Mather & Platt. *BP* 733,256

The gearing and mechanism which effect rail width adjustment of the stenter are placed outside the casing and the push-pull rods which are the connections pass through holes in the casing. This obviates many of the troubles and difficulties which occur when impregnated fabrics are being treated in the stenter. C. O. C.

Fabric Dryer. C. Kamprath. *USP* 2,691,225

Machine in which the supply of drying air is applied to the fabric under closely controlled conditions so as to ensure even drying occurs the width of the fabric. C. O. C.

Drying Paper, Cloth, etc. J. S. Daniels. *USP* 2,689,196

Machine in which coated paper or the like passes through with its moist portions arranged in several runs in which the paper travels vertically. The wet portions are supported entirely free of harmful contact with surfaces foreign to the paper. C. O. C.

Compressive Shrinking of Fabric. Trubenised (Gt. Britain). *BP* 733,384

The cloth is placed lengthwise upon a member one end of which is mounted on a rotating shaft. The cloth is closely confined between two surfaces extending radially from the shaft so that it cannot move except in its own plane. The shaft is then rotated while preventing movement of the outer end of the cloth. The centrifugal force set up compresses and shrinks the cloth. C. O. C.

Screen Printing Apparatus having a Mechanically Operated Squeegee. John Wheelwright & Co. *BP* 733,643

Pre-setting Machine. N. Corah & Sons. *BP* 733,377

Knitted garments are mounted on forms carried by a continuous conveyor through a steaming followed by a drying zone. A rotatably mounted door closes the steam chamber during treatment of the garments. G. E. K.

Finishing Nylon Hose. K. Frowein and F. Voss. *BP* 732,993

Nylon hose mounted on forms pass successively on an endless conveyor through pre-setting, dyeing and post-setting processes. Damage due to excessive manual handling is thereby minimised. G. E. K.

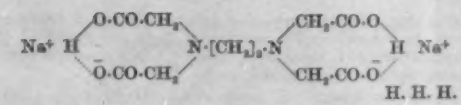
Setting Nylon Hose. Paramount Textile Machinery Co. *USP* 2,689,071

Apparatus in which one set of forms is accessible to the operator while the other set is in the setting chamber. The door is on the outside of the chamber thus enabling the volume of the chamber to be just that required to accommodate a set of forms and so reducing the amount of steam necessary for each setting operation. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Infrared Spectra of Ethylenediaminetetra-acetic Acid and its Di- and Tetra-sodium Salts. D. Chapman. *J.C.S.*, 1766–1769 (June 1955).

The infrared spectra of the title compounds are obtained between 650 and 3500 cm.$^{-1}$; they do not support the mode of ionisation of the acid previously suggested. The spectrum of the disodium salt suggests the presence of both carboxylic acid and carboxylate ion groups in the mol., whereas only carboxylate groups should occur. The new structure proposed for the disodium salt is—



H. H. H.

Organic Anti-foaming Agents. C. L. Agre, G. Dinga, and R. Pflaum. *J. Org. Chem.*, **20**, 695–699 (June 1955).

PATENTS

Inhibiting Tarnishing of Metals by Detergents. Ilford. *BP* 722,332

The tendency for metals to be tarnished by detergents, particularly alkaline detergents and those containing calcium-sequestering phosphates, is inhibited by addition of a compound of formula—

(R = H, Alk, aralkyl, subst. or unsubst. Ar), e.g. 1(α-naphthyl)-5-mercapto-1:2:3:4-tetrazole. C. O. C.

Textile Lubricant. American Viscose Corpn. *USP* 2,690,427

An emulsion containing a compound of formula—

$$X(R^1O)_nR^2$$

(X = H, OH or Alk of 1–6 C; R^1 = CH_2 or C_2H_4; n = 2–6; R^2 = acyl of 12–30 C; C atoms in R^2 : n × C atoms in R^1 + C atoms in X :: ≮ 2:1, and as emulsifying agent an ethylene oxide condensate of a mono-anhydrohexitol with a satd. fatty acid of 14–18 C. Thus an emulsion for lubricating rayon cakes consists of Butyl Cellosolve stearate (0·2%), condensate of 1 mol. sorbitan tristearate with ethylene-oxide (12 mol.) (0·2), Na sorbitol maleate (0·05), water (to make to 100). These emulsifying agents themselves act as lubricants. C. O. C.

Wool Oiling Composition. K. Bougartchev. *BP* 733,619

A wool oil composition comprises a homogeneous blend of a mineral oil, a neutralised sulphonated vegetable oil, a polyether alcohol, e.g. Triton 100 (Rohm & Haas) with or without a lower aliphatic alcohol (≯ 5 C atoms), and a metal or ammonium soap, which may be made by saponifying an olein *in situ* in the course of preparing the blend. J. W. B.

Sizes Containing Copolymers. Monsanto. *BP* 733,507

Sizes particularly suitable for regenerated cellulose and cellulose acetate yarns comprise a copolymer containing 90–98 mol. % of combined vinyl acetate and 10–2 mol. % of an unsaturated organic compound copolymerisable with vinyl acetate and containing 3–9 C atoms/molecule and having at least 1 free —COOH group, e.g. crotonic acid, or alkali metal salts of such a copolymer. It must have, in molar solution in 99·5% w/w ethanol and 0·5% w/w benzene, a viscosity < 18 c.p. at 20°c. The production comprises gradually adding the monomers to an aqueous solution in the presence of ≮ 1% w/w of a catalyst, e.g. benzoyl peroxide, and ≮ 0·11% of a water soluble protective colloid suspending agent e.g. dioctyl ester of sulphosuccinic acid, the copolymerisation being carried out so that the product is in bead form.

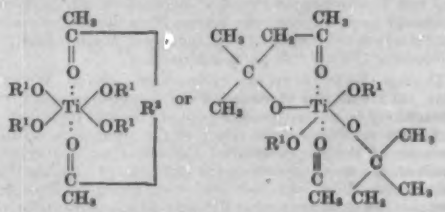
A solution suitable for adding to the size box of a slasher is produced by vigorously agitating the copolymer beads with a solution of Na_2CO_3, $NaHCO_3$, or NaOH. J. W. B.

Size for Glass Fibres. Libbey–Owens–Ford Glass Co. *USP* 2,688,007

An aqueous mixture of a hydrolysed alkenyl silicone ester, a film-forming thermoplastic resin and a cationic lubricant is a very good size for glass fibres. C. O. C.

Stable Complex Titanic Acid Esters and their Reaction with High Molecular Weight Compounds containing Hydroxyl Groups. FBy. *BP* 734,113–4

A simple tetra-alkyl or tetrachloroalkyl orthotitanate is treated with an aliphatic hydroxyketone, an aliphatic hydroxy aldehyde or an aliphatic keto compound which reacts readily as an unsatd. hydroxyketone in its enolic form, e.g. diacetone alcohol or acetoacetic ester to yield complex esters which may have either of the following formulae—



Added to solutions of high mol. wt. compounds containing hydroxyl groups, e.g. cellulose nitrate or polyhydroxyl alcohol–polybasic acid condensates, they have no immediate effect but on heating they act as cross linking agents. C. O. C.

Aqueous Emulsions of Acrylic Ternary Polymers. Ciba. *BP* 733,428

Stable, acidic, aqueous emulsions are obtained by emulsifying in presence of an emulsifying agent an ester of an acid of formula—

$$CH_2{:}CR{\cdot}COOH$$

(R = H or Alk) e.g. acrylic acid, and a nitrile of such an acid, e.g. methacrylic nitrile together with a small proportion of a free singly unsatd. monocarboxylic acid capable of being copolymerised, e.g. crotonic acid. They are useful for coating textiles and paper without the use of thickening agents. C. O. C.

***NN'*-Di(2-chlorophenyl)-ethylene Diamine as Gas Fume Fading Inhibitor.** Celanese Corpn. of America. *USP* 2,691,565

*NN*¹-Di-(2-chlorophenyl)-ethylene diamine is substantive to organic derivatives of cellulose and is an excellent gas fume fading inhibitor which does not discolour on exposure to gas fume. The protection given is fast to dry cleaning, washing and light. C. O. C.

Heat Stabiliser for Polyacrylonitrile Solutions. DuP. *USP* 2,689,236

Solutions of acrylonitrile polymers in dimethylformamide or similar solvent are given improved resistance to becoming coloured when heating by adding 0·1–2·0% (on the wt. of the polymer) of an organic anhydride and as much of a sulphhydryl containing substance, e.g. acetic anhydride and thiosorbitol. C. O. C.

Plasticised Polyvinyl Chloride Compositions for Coating Book Cloths. DuP. *BP* 733,605

A mixture of a polyvinyl chloride or similar resin with castor oil maleate produces a coating on book cloth which can be lithographically printed. C. O. C.

Plasticised Polyvinyl Chloride Compositions for Fabric Coating. DuP. *USP* 2,690,981

A composition specially suitable for coating book cloths is obtained by plasticising polyvinyl chloride with a mixture of tricresyl phosphate and poly-α-methylstyrene. This yields a coating to which drying oil inks will firmly adhere. Addition of an aryl sulphonamide–formaldehyde resin improves the flex durability, gloss and resistance to marring of the coating. C. O. C.

Dispersions of Acrylonitrile-*N*-vinyllactam Copolymers— Coating Compositions. Celanese Corpn. of America. *BP* 733,601

An acrylonitrile-*N*-vinyllactam copolymer dispersed in a homogeneous mixture of a solvent and a non-solvent yields a coating composition suitable for application to textiles. C. O. C.

Rotproofing Agents. C. J. Faulkner. *BP* 734,119

Compounds of formula—

$$SnR^1R^2R^3X$$

(R^1, R^2 and R^3 = same or different organic groups linked to the Sn atom by a C atom; X = a monovalent inorganic or organic group linked to the Sn atom by other than a C atom), e.g. tin triisopropylhydroxide, are excellent rotproofing agents for textiles, leather, paints, etc. C. O. C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

p-Nitrosoaniline. J. Willenz. *J.C.S.*, 2049 (June 1955).

p-Nitrosoaniline was claimed by Fischer and Hepp to be formed in 50% yield by heating *p*-nitrosophenol (1 part) with NH_4Cl (5 parts), dry CH_3COONH_4 (10 parts), and a little ammonium carbonate (Fischer and Hepp, *Ber.*, **20**, 2474 (1887)). Attempts to repeat this prep. using pure reactants in glass apparatus were unsuccessful, but reaction in an iron crucible in presence of $FeCl_3$ as catalyst afforded *p*-nitrosoaniline in ~ 34% yield. H. H. H.

Preparation of Some *N*-Alkyl- and *NN*-Dialkyl-*p*-nitrosoanilines. J. Willenz. *J.C.S.*, 1677–1682 (June 1955).

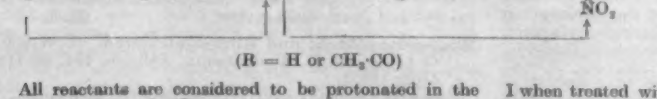
The prep. of the *p*-nitroso deriv. from *N*-*iso*propyl-, *N*-*n*-hexyl-, *N*-3:5:5-trimethylhexyl-, and *N*-*n*-octadecyl-aniline, and from *NN*-di-*n*-hexyl-, *N*-*n*-hexyl-*N*-methyl-, *NN*-bis-(3:5:5-trimethylhexyl)-, and *N*-ethyl-*N*-3:5:5-trimethylhexyl-aniline are described. Attempted Fischer–Hepp rearrangement of *N*-nitroso-*N*-*n*-octadecylaniline resulted in denitrosation. It has been claimed that the direct nitrosation reaction fails if the alkyl groups are large (*see* Sidgwick, *The Organic Chemistry of Nitrogen* (1942), p. 218), but no difficulty was experienced in direct introduction of a *p*-nitroso group into any of the above dialkylanilines, which include several with very bulky substituents. H. H. H.

Physical Constants of 3-Nitro-2-naphthylamine. A. Bryson and R. L. Werner. *Chem. and Ind.*, 947 (23 July 1955).

The physical constants of the 3-nitro-2-naphthylamine described by Hodgson and Turner which has since been shown to be a mixture of 5 and 8-nitro-2-naphthylamines are now invalid. Examination of a sample of 3-nitro-2-naphthylamine supplied by Prof. Verkade has shown that it is 200 times stronger as a base than is 1-nitro-2-naphthylamine (pK. at 25°c. 1·48). The UV absorption spectra of the free base and of the 3-nitro-2-naphthylammonium ion have been examined and the infrared stretching frequencies for the NH-bond determined in carbon tetrachloride solution. C. H. R.

Migration of Aromatic Nitro Groups. K. H. Pausacker and J. G. Scroggie. *J.C.S.*, 1897–1899 (June 1955).

2:3-Dinitroacetanilide, 2:3-dinitroaniline, and 2:3-dinitrophenol undergo rearrangement when heated with conc. H_2SO_4, whereas the corresponding 2:5- and 3:4-disubstituted cpd. do not. The following mechanism is proposed for the rearrangement—



(R = H or CH_3·CO)

All reactants are considered to be protonated in the H_2SO_4 medium; the first stage is the conversion of the 2:3-dinitro-cpd. into the corresponding 3:*N*-dinitro-cpd. H. H. H.

Catalytic Oxidation of Phenanthrene. J. D. Brooks. *J. Appl. Chem.*, **5**, 250–260 (June 1955).

In view of the possibility that phenanthrene, which, after naphthalene, is the most abundant single component of high-temp. coal tar, could yield valuable chemical intermediates by a suitable oxidation treatment, an examination is made of its vapour-phase oxidation by air in presence of "fluidised" silica–vanadium oxide catalysts. The main products are phthalic anhydride, 2′-hydroxydiphenyl-2-carboxylic acid lactone, and 1:2-naphthalic anhydride. No suitable large-scale methods for preparing the second and third products have hitherto been available. A. E. S.

Constitution and Light Absorption. VII—Effect of Phenyl Chromophores on the Light Absorption of Cumulenes. F. Bohlmann and K. Kieslich. *Chem. Ber.*, **88**, 1211–1218 (Aug. 1955).

Reaction of Aromatic Fluoro Compounds with Phenyllithium. R. Huisgen and H. Rist. *Annalen*, **594**, 137–158 (July 1955).

1-Fluoronaphthalene reacts with phenyllithium to yield on carboxylation 2-phenyl-1-naphthoic acid (I; 45%) and 1-phenyl-2-naphthoic acid (II; 26%), whereas 2-fluoronaphthalene similarly leads to I (20%), II (10%), and 2-phenyl-3-naphthoic acid (20%). In the same way is obtained from *o*-fluoroanisole 3-methoxydiphenyl-2-carboxylic acid (III; 61%) and 2-methoxydiphenyl-6-carboxylic acid (IV; 4%); i.e. by far the greater part of the phenyl residue does not appear in the position from which fluorine has been removed ("cinesubstitution"). *m*-Fluoroanisole gives III (72%) and IV (1·6%). A common intermediate in both sets of reactions is therefore postulated, the latter being formulated as—

H. E. N.

Bisulphite Compound of 1-Naphthol. 7-Nitro-1-naphthol. N. N. Karandasheva and S. V. Bogdanov. *J. Gen. Chem. U.S.S.R.*, **25**, 1152–1156 (June 1955).

Bucherer (*Z. Farben- und Textil-Chemie*, **1**, 478 (1902)) assumed that the conversion of a hydroxynaphthoic acid into the corresponding naphthol by treatment with sodium bisulphite proceeds through the formation of a bisulphite cpd., its decarboxylation, and the conversion of the resulting bisulphite cpd. of the naphthol into the naphthol itself. He found that 2-hydroxy-1-naphthoic and 3-hydroxy-2-naphthoic acids give 2-naphthol as sole product, whereas 1-hydroxy-2-naphthoic acid (I) gives a mixture of 1-naphthol (II) and the bisulphite cpd. of 1-naphthol (III). The last reaction is now re-examined, and it is found that II is formed as a ppt. in the early stages of the reaction and then dissolves gradually as a result of its conversion into III, so that Bucherer's sequence is incorrect. III is isolated in the pure state ($C_{10}H_7OH$,$NaHSO_3$,H_2O). It is readily converted into 1-naphthylamine by treatment with ammonium sulphite at 60°c. It is unstable to alkali, which converts it into II, but it is stable to acids and can be nitrated in conc. H_2SO_4 soln. at 0°c. Treatment of the nitrated bisulphite cpd. with NaOH soln. liberates a mixture of 7- and 5-nitro-1-naphthols, the former (isolated for the first time) predominating. A. E. S.

Preparation of Azotol A from a Mixed Anhydride of Silicic and 3-Hydroxy-2-naphthoic Acids. A. V. Kirsanov, E. S. Levchenko, and G. S. Tret'yakova. *Ukrain. khim. zhur.*, **19**, 504–507 (1953): *Referat. zhur.* (*Khim.*), No. 23410 (1954): *Chem. Abs.*, **49**, 8229 (25 June 1955).

In the preparation of 3-hydroxy-2-naphthanilide (I) (Azotol A, i.e. Naphtol AS) PCl_5 can be replaced by $SiCl_4$. With 3-hydroxy-2-naphthoic acid (II), $SiCl_4$ yields a yellow polymeric mixed anhydride of II and silicic acid $[(O\text{-}C_{10}H_6\text{·}COO)_4Si]_x$ (III), which gives I when treated with aniline. The product contains SiO_2 and is purified by reprecipitation from alkaline soln. It is not necessary to isolate III. When $SiCl_4$ and aniline are present in excess, some 3-hydroxy-*NN′*-diphenyl-2-naphthamidine is formed in addition to I. A. E. S.

Amino Derivatives of Triarylmethanols. O. F. Ginzburg and N. S. Melnikova. *J. Gen. Chem. U.S.S.R.*, **25**, 1156–1160 (June 1955).

Extension of previous work on dissociation const. (see J.S.D.C., **70**, 198 (1954)) to other deriv. of Malachite Green (having 2- and 3-methoxy and 3- and 4-nitro in the previously unsubstituted phenyl group). A. E. S.

Azo Derivatives of Benzothiazole. A. I. Kiprianov and I. P. Fedorova. *Ukrain. khim. zhur.*, **21**, 76–80 (1955): *Chem. Abs.*, **49**, 8926 (10 July 1955).

The NH_2 group of 6-amino-2-methylbenzothiazole is replaced by R·N:N– by the action of R·NO in glacial acetic acid, and the absorption spectra of some of the resulting dyes are determined in alcoholic soln. (R = phenyl (principal max. 337 mμ.), *p*-nitrophenyl (354 mμ.),

p-tolyl, *p*-chlorophenyl (343 mμ.), methoxyphenyl (359 mμ.), 6-benzothiazolyl, *p*-hydroxyphenyl (365 mμ.), 2-hydroxy-1-naphthyl, *p*-dimethylaminophenyl (425 mμ.), and 2-methyl-6-benzothiazolyl). 6:6′-Azobenzothiazole is prepared in an analogous way. A. E. S.

Thiazoles. XXV— Grignard Reaction of 2-Phenylazothiazoles. H. Beyer, C.-F. Kröger, and M. Zander. *Chem. Ber.*, **88**, 1233–1237 (Aug. 1955).

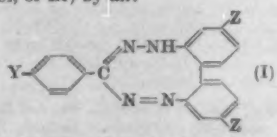
The 4-phenyl, 4:5-diphenyl, and 4:5-dimethyl deriv. of 2-phenylazothiazole react with phenylmagnesium bromide to form the corresponding *NN*-diphenyl-*N*′-2-thiazolylhydrazines, which are also synthesised. With the 4-methyl deriv. the reaction proceeds further yielding a blue resin, which is identified as an oxidation product of the corresponding hydrazine. The 4-phenyl deriv. also gives a blue oxidation product. 4:4′:5:5′-Tetramethyl-2:2′-azothiazole is prepared. H. E. N.

Photo-oxidation of Dyes in Presence of Hydrogen Peroxide. C. M. Desai and B. K. Vaidya. *J. Indian Chem. Soc.*, **32**, 252–253 (April 1955).

The rates of fading of dye and decomposition of hydrogen peroxide have been measured when soln. of Binschedler's Green, Malachite Green, Crystal Violet, Rosaniline, picric acid, Naphthol Yellow, Chrysoidine, and aminoazobenzene ($0{\cdot}25-2{\cdot}0\times10^{-6}$M.) in aqueous hydrogen peroxide ($2{-}4\times10^{-4}$M.) were exposed to sunlight, allowance being made for the simultaneous thermal reactions. The fading of the dyes, after an induction period, at first increases with time and then diminishes: it is accelerated 5–10 fold by H_2O_2. The decomposition of H_2O_2 is inhibited by the dyes in the order: basic dyes and Chrysoidine > aminoazobenzene > Naphthol Yellow > picric acid. There is some dependence of the induction period on the composition of the soln. A. J.

Cyclic Formazans. D. Jerchel and W. Edler. *Chem. Ber.*, **88**, 1284–1295 (Aug. 1955).

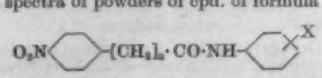
These are synthesised as follows— arylnitromethanes are coupled to diazotised 2-amino-2′-nitrodiphenyls, the products hydrogenated to the corresponding diaminohydrazones and oxidised to the formazans (I: Y = H or Cl; Z = H, Cl, or Br) by air.



Their colour is brown-yellow (the non-cyclic formazans are deep red) and they do not form deeply coloured complexes with copper acetate. The corresponding cpd. with a seven-membered ring obtained from diazotised *o*-nitroaniline is red and very sensitive to acid. H. E. N.

Separated Chromophoric Systems. XXVII— Colour of Arylamides of 4-*p*-Nitrophenylbutyric Acid. XXVIII— Comparative Study of the Absorption Spectra of Arylamides of *p*-Nitrophenylacetic, *p*-Nitrohydrocinnamic, 4-*p*-Nitrophenylbutyric, and *p*-Nitrobenzoic Acids. E. A. Smirnov. *J. Gen. Chem. U.S.S.R.*, **25**, 802–809 (April); 1014–1021 (May 1955).

XXVII— A comparative study is made of the visible reflection spectra of powders of cpd. of formula I—



(n = 1, 2, and 3; X = O·CH_3, OH, and N(CH_3)$_2$, oriented *meta* and *para*). The cpd. I (n = 1) and I (n = 2) have been investigated previously (cf. J.S.D.C., **66**, 489 (1950); for related work of same school, see J.S.D.C., **71**, 192 (April 1955)). The cpd. I (X = O·CH_3) are colourless, I (X = OH) are colourless to pale yellow, and I (X = N(CH_3)$_2$) are yellow to orange. Compounds I (n = 1) and I (n = 3) are very similar in colour and absorb at shorter wavelengths than I (n = 2). The presence of a chain of three methylenes in I (n = 3) excludes all possibility of tautomeric change resulting in the creation of a continuous system of alternating double bonds extending from NO_2 to NH·Ar, although such a change is possible for the I (n = 2) cpd. The colour of I (n = 3) must therefore be attributed to direct, external interaction between separated electron-donating and electron-accepting chromophoric systems.

XXVIII— In a further study of the cpd. I (n = 1, 2, and 3), their ultraviolet and visible absorption spectra are determined in dil. alcoholic soln. (10^{-6}–10^{-5}M.) and are compared with the spectra of the cpd. I (n = 0). It is shown that the effects detected in the solid state (see above) are very feeble in dil. soln., which provides further evidence that these effects are attributable to intermolecular action. When X is *para* to NH all the cpd. have a short-wave max. at 250–280 mμ. and when X is *meta* to NH they have two short-wave max. in the same region separated by ~ 40 mμ. The positions of these max. depend much more on the identity of X than on the value of n. When n = 1, 2, and 3, the spectra can be closely reproduced by summation of curves for pairs of cpd. containing the component chromophoric systems (*p*-NO_2·C_6H_4·CH_3 and CH_3·CO·NH·C_6H_4·X), but when n = 0 this cannot be done— in particular, the latter cpd. give also a long-wave max. associated with intramolecular action through the CO·NH (or C(OH):N) grouping. Nevertheless, some of the cpd. I (n = 1, 2, and 3) show slight departures from additivity and appreciable departures from Beer's law as the concn. is increased; these observations indicate that some intermolecular action occurs between the chromophoric systems, even in dil. soln. A. E. S.

Benzothiazolylthiacyanines. I. K. Ushenko. *Soobshcheniya nauch. rabotakh Vsesoyuz. khim. obshchestva im. Mendeleeva*, No. 2, 1–4 (1953): *Referat. zhur. (Khim.)*, No. 30590 (1954): *Chem. Abs.*, **49**, 8265 (25 June 1955).

Colour Reactions of Unsaturated Carbonyl Compounds— III. S. Hünig and J. Utermann. *Chem. Ber.*, **88**, 1201–1204 (Aug. 1955).

***NN*-Dimethyl-*p*-benzoquinone-di-imonium Diperchlorate.** S. Hünig and W. Daum. *Chem. Ber.*, **88**, 1238–1241 (Aug. 1955).

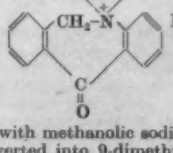
Willstätter and Piccard's preparation of the dinitrate (*Ber.*, **41**, 1473 (1904)) could not be repeated. However, the diperchlorate is obtained simply by dissolving the black-green perchlorate of Wurster's Red in acetic acid containing perchloric acid. Soon the soln. becomes decolorised and a pale ppt. of the required cpd. separates, *p*-aminodimethylaniline remaining in soln. Similarly, it can be obtained by adding a soln. of *p*-aminodimethylaniline in acetic acid to a soln. of an excess of chromic acid in acetic acid-perchloric acid. H. E. N.

Behaviour of Unsaturated Ammonium Salts towards Proton Acceptors (Preparation of Anthraquinone and Methylaniline). G. Wittig and H. Sommer. *Annalen*, **594**, 1–14 (July 1955).

Among the several reactions studied is that between 1-*N*-methylanilinobuta-1:3-diene and naphthaquinone in ether under nitrogen, which yields anthraquinone (89% of theory) and methylaniline (40%). H. E. N.

Ring-enlargement and Ring-contraction. G. Wittig, G. Closs, and F. Mindermann. *Annalen*, **594**, 89–118 (July 1955).

Amongst the many expt. reported are the following—



I on treatment with methanolic sodium methoxide under nitrogen is converted into 9-dimethylaminoanthr-10-one, which is synthesised in 10% yield by the reaction of 9-chloroanthr-10-one with lithium dimethylamide under nitrogen. It decomposes into anthraquinone on standing in air after some days, more quickly in methanolic KOH. A similar reaction using 9-bromoanthracene leads to 62% of 9-dimethylaminoanthracene, which on standing in air forms anthraquinone. Its dihydro deriv., obtained using sodium amalgam and ethanol under nitrogen, is stable to air and 5% methanolic KOH. H. E. N.

Anthraquinone Derivatives. XXIV—Hydrolysis of Anthraquinone-1-sulphonic Acid with Replacement of the Sulpho Group by Hydroxyl. V. V. Kozlov and A. A. Egorova. *J. Gen. Chem. U.S.S.R.*, **25**, 997–1003 (May); **XXV—Hydrolysis of Anthraquinone-1:8-disulphonic Acid.** V. V. Kozlov. *Ibid.*, 1206–1212 (June 1955).

XXIV—In the preceding communication (see J.S.D.C., **71**, 474 (Aug. 1955)) it was shown that, even in absence of Hg salts, hydrolysis of anthraquinone-1-sulphonic acid to anthraquinone can be effected under sufficiently severe conditions (70–80% H_2SO_4, 190–230°C.). It is now shown that when water or dil. H_2SO_4 is used as hydrolysing agent at the same temp. the product is 1-hydroxyanthraquinone (or a mixture of this with anthraquinone at higher concn. of H_2SO_4). Addition of a small amount of $HgSO_4$ (1% on the wt. of sulphonic acid) to the reaction mixture does not affect the direction of the reaction, but addition of 5% of $HgSO_4$ results in the formation of anthraquinone as sole product.

XXV—The results of experiments on the hydrolysis of anthraquinone-1:8-disulphonic acid are very similar to those obtained for the 1-sulphonic acid, one or both sulpho groups being replaceable by hydrogen or hydroxyl with formation of all theoretically possible products. As before, addition of Hg salts promotes replacement of the sulpho group by hydrogen. Hydrolysis in 0·25% H_2SO_4 for 6 hr. at 260°C. gives a quantitative yield of 8-hydroxyanthraquinone-1-sulphonic acid. A. E. S.

Polycyclic Quinones. I—Synthesis of Tetramethylindanthrone. N. S. Dokunikhin and T. N. Kurdyumova. *Sbornik statei obshchei khim.*, **2**, 1411–1417 (1953): *Chem. Abs.*, **49**, 5491 (25 April 1955).

Nitration of *o*-(3:4-dimethylbenzoyl)benzoic acid followed by reduction of the product results in the formation of a mixture of monoamino deriv., from which *o*-(2-amino-3:4-dimethylbenzoyl)benzoic acid is readily removed in the form of its lactam. The other component, *o*-(5-amino-3:4-dimethylbenzoyl)benzoic acid, is converted by treatment with 93–96% H_2SO_4 into a mixture of 1-amino-2:3-dimethyl- and 2-amino-3:4-dimethyl-anthraquinones, which are separated chromatographically. The latter cpd. is brominated, and the 2-amino-1-bromo-3:4-dimethyl-anthraquinone obtained is converted into 3:3′:4:4′-tetramethylindanthrone by treatment with sodium acetate, MgO, and CuO in trichlorobenzene at 180°C. A. E. S.

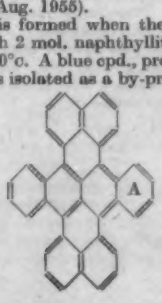
Calculated Bond Lengths in some Cyclic Compounds. I—Methods of Calculation. T. H. Goodwin and V. Vard. *J.C.S.*, 1683–1688 (June 1955).

II—Benzanthrone, Acedianthrone, and Flavanthrone. T. H. Goodwin. *J.C.S.*, 1689–1694 (June 1955).

Methods are developed in I for expanding secular determinants and solving the resulting equation for the energy levels in molecular-orbital calculations of bond orders, and a new curve for correlating bond order and bond length is proposed. These methods are now employed in association with the molecular-orbital method to derive the energy levels, bond orders, and bond lengths, in benzanthrone, acedianthrone, and flavanthrone. Bond orders and bond lengths in benzanthrone are also derived by the two simple valence-bond approximations of I. For the second and the third compound the observed and the calculated interatomic distances agree very satisfactorily within the experimental uncertainty except for a very few bonds. H. H. H.

Aromatic Hydrocarbons. LXIX—7:8-15:16-Dibenzoterrylene. E. Clar and W. Willicks. *Chem. Ber.*, **88**, 1205–1207 (Aug. 1955).

This cpd. (I) is formed when the reaction product of naphthacene with 2 mol. naphthyllithium is treated with NaCl–$AlCl_3$ at 120°C. A blue cpd., probably the tetrahydro deriv. (ring A), is isolated as a by-product.



(I)

I is obtained in deep green needles, m.p. 460°C. (evacuated capillary). It yields green solutions, which are relatively stable to photo-oxidation, though a yellow adduct is formed with maleic anhydride. H. E. N.

PATENTS

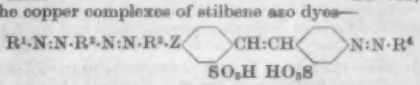
Trisazo Direct Cotton Dyes for After-coppering. Ciba. *BP* 733,361

Aminodisazo compounds—

(R^1 = residue of an *o*-hydroxybenzoic acid; R^2 = aryl of benzene series in which the azo links are *para* to each other, containing OAlk *ortho* to the azo link between R^2 and the naphthalene nucleus) are diazotised and coupled with 8-hydroxyquinoline to give direct cotton dyes suitable for coppering in the dyebath or on the fibre. Thus the aminomonoazo compound 5-aminosalicylic acid → *p*-cresidine is diazotised and coupled with *N*-(*p*-amino-*m*-sulphophenyl)-J acid in presence of soda ash. The aminodisazo compound so formed is then diazotised and added to an acid solution of 8-hydroxyquinoline, coupling being completed by adding soda ash. The product dyes cotton greenish navy by the aftercoppering process. E. S.

Metal(Copper)-complex Polyazo Direct Cotton Dyes. Ciba. *BP* 733,354

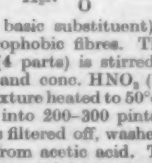
The copper complexes of stilbene azo dyes—



(R^1 and R^2 = benzene residues, one containing OH and the other either OH or OCH_3 in *ortho* positions to the azo link; R^3 = a benzene residue in which Z and the azo link are *para* to each other; R^4 = a salicylic acid residue coupling *para* to the OH group, or the residue of an alkoxybenzene; Z = azo or azoxy) are brown and olive direct cotton dyes. Thus the stilbene dyestuff obtained by coupling diazotised 4-amino-4′-nitrostilbene-2:2′-disulphonic acid with phenol, and methylating the OH group with methyl chloride, is boiled with the aminodisazo dye 2-aminophenol-4-sulphonic acid → *m*-anisidine → *m*-toluidine in aq. NaOH. The condensation product so formed is heated with ammoniacal copper sulphate in presence of ethanolamine to give the complex, which dyes cotton brown. E. S.

Dyes for Hydrophobic Fibres. DuP. *USP* 2,687,939

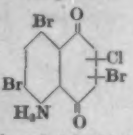
Dyes of formula—



(X = a neutral or basic substituent) have good dyeing properties for hydrophobic fibres. Thus 2:3-dimethyl-1:4-naphthoquinone (4 parts) is stirred into a mixture of conc. H_2SO_4 (50·4) and conc. HNO_3 (16·8) at room temperature and the mixture heated to 50°C. for 1 hr. It is then cooled and poured into 200–300 pints of ice water. The yellow precipitate is filtered off, washed free of acid, dried and recrystallised from acetic acid. The product (6·3) is added to a solution containing water (356), NaOH (45·4) and Na hydrosulphite (38) at 26–34°C. over 10 min., stirred for a further 15 min., a little nitrobenzene sodium sulphonate added and air bubbled through until complete oxidation is obtained. The resulting red slurry is stirred for a further 30 min., washed with cold water till free of alkali, dried and recrystallised from an aliphatic hydrocarbon of b.p. 120°C. The resulting 2:3-dimethyl-5-amino-1:4-naphthaquinone (10) is dissolved in glacial acetic acid (105) and Br (31·2) in glacial acetic acid (21) added over 30 min. at 25°C. The mixture is stirred at room temperature for 24 hr. It is then poured into ice water (400) with vigorous stirring. The red precipitate is stirred for 1 hr., filtered off, washed free of acid with cold water, dried and recrystallised from ethanol. The purified 6:8-dibromo-5-amino-2:3-dimethyl-1:4-naphthoquinone so produced dyes **Terylene orange.**

USP 2,687,940

5-Amino-2:3-dichloro-1:4-naphthoquinone when intensely brominated, e.g. by treatment with an acetic acid solution of Br on a water bath, introduces two Br atoms into the 6 and 8 positions and replaces one of the Cl atoms by Br thus yielding the compound—



which dyes Terylene deep bright bluish red and also dyes cellulose acetate, nylon and acrylonitrile fibres.

C. O. C.

Blue Disperse Dyes Fast to Gas Fume Fading. Celanese Corpn. of America. *USP* 2,687,941

5-Amino-8-hydroxy-1:4-naphthoquinone-1-imine when condensed with a hydroxy alkyl amino benzene, e.g. *m*-aminobenzyl alcohol, yields greenish blue disperse dyes of improved resistance to gas fume fading. C. O. C.

β-Hydroxyalkylthio-anthraquinone— Disperse Dyes. Celanese Corpn. of America. *USP* 2,672,464

1:5-Dihydroxy-4:8-diamino- and 1:8-dihydroxy-4:5-diamino-anthraquinones containing $-SO_3H$ in one or both β-positions to OH are condensed with a mercapto-alkyl alcohol to give blue disperse dyes which are not sensitive to the concentration of detergent in the dyebath. Thus, 4:8-diamino-1:5-dihydroxyanthraquinone-2-sulphonic acid is refluxed for 5 hr. with mercapto-ethanol and aq. NaOH.

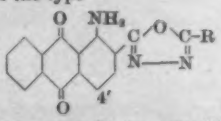
R. K. F.

Halogeno-1:4-bis-Trialkylphenylaminoanthraquinone Sulphonic Acids— Neutral Dyeing Acid Dyes. S. *BP* 733,458

Chlorine or bromine is introduced into the 6 and/or 7 positions of 1:4-bis-2′:4′:6′-trimethyl (or -triethyl)phenylaminoanthraquinone sulphonated in both 3′-positions by treating with the halogen in H_2SO_4 solution. Alternatively the halogen is added to the sulphonation mixture directly following sulphonation. The resulting dyes have good neutral dyeing properties and are fast to milling and light. Thus 1:4-bis-2′:4′:6′-trimethylphenylaminoanthraquinone is sulphated with oleum in H_2SO_4 at 38–40°c. When a test sample is completely soluble, the mixture is cooled to 0°c. and 65% oleum, followed by bromine, added. Stirring is continued at this temperature for 5 hr., the whole poured into ice and water and salted out. R. K. F.

Diamino-Anthraquinonyl-Oxadiazoles. FBy. *BP* 733,456

Compounds of the type—

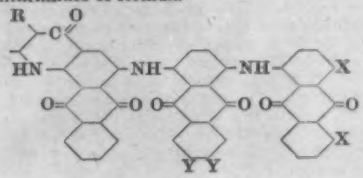


where R = an organic radical, preferably vattable, are nitrated with conc. HNO_3 and reduced to introduce a 4′-NH_2. Where R contains a 1″-amino anthraquinonyl a 4″-NH_2 is also inserted. Thus 2:5-bis-(1′-amino-2′-anthraquinonyl)-1:3:4-oxadiazole is added to HNO_3, (45°Bé.), from which HNO_3 has been removed by adding urea, while cooling with ice water. The temperature is then raised to 35–40°c. until the original red dye is all converted into the colourless nitramino-nitro compound, which is separated and reduced with aq. Na_2S at 90–100°c.

R. K. F.

Acridone-Phthaloyl-Carbazoles— Vat Dyes. Ciba. *BP* 733,372

Trianthrimides of formula—



where R = aromatic residue; one X = H, the other X = H or acylamino; Y = H or Hal) are cyclised to give the corresponding bis-carbazoles which are green to olive vat dyes, fast to light, chlorine and bucking. Thus the trianthrimide made by heating at 210°c. for 10 hr., 4-chloro-1:1′-dianthrimide and 4-aminoanthraquinone-2:1(*N*)-benzacridone in nitrobenzene containing Na_2CO_3 and Cu_2Cl_2, is heated at 140°c. for 1 hr. in a solvent medium of $AlCl_3$ and pyridine. Separation is effected by pouring into water.

R. K. F.

Perylene Tetracarboxylic Acid bis-Arylimide Vat Dyes. General Aniline. *USP* 2,668,815

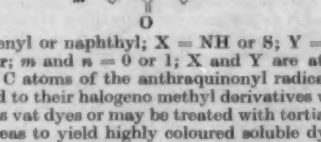
3:4:9:10-Perylene-tetracarboxylic acid or its anhydride is condensed with an acylaminophenylamine, or alternatively a perylene-tetracarboxy-bis-aminophenylamine is acylated, to give bright red light and chlorine-fast vat dyes of formula—

(R^1 and R^3 = monocyclic aryl; R^2·CO and R^4·CO = same or different acyl). Thus, 3:4:9:10-perylene-tetracarboxylic acid anhydride is heated with *N*-acetyl-*p*-phenylene diamine in phenol at 180°c., cooled, diluted with methanol and filtered. Unreacted perylene tetracarboxylic acid is washed out of the resulting product with 2% aq. NaOH.

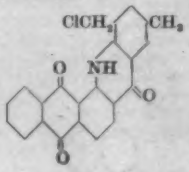
R. K. F.

Halogenomethyl Derivatives of the Acridone and Thioxanthone Series— Vat Dyes and Intermediates therefor. General Aniline. *USP* 2,691,022

Dyes of formula—



(R = phenyl or naphthyl; X = NH or S; Y = CO; Z = Alk or Ar; *m* and *n* = 0 or 1; X and Y are attached to adjacent C atoms of the anthraquinonyl radical) may be converted to their halogeno methyl derivatives which may be used as vat dyes or may be treated with tertiary amines or thioureas to yield highly coloured soluble dyes having affinity for cotton. When they are vatted these dyes yield the corresponding methyl compounds which are much brighter on cotton than the methyl derivatives obtained by caustic fusion of the chloromethylated acridones and thioxanthones. The developed colours are yellow to violet and are faster and brighter than those obtained with the starting materials. Thus anthraquinone-5′-methyl-1:2-acridone (34), 96% H_2SO_4 (368) and bischloromethyl ether (33) are mixed and kept at room temperature for three days. They are then poured into ice water, and the product filtered off, washed free from acid and dried at 60°c. It is a dye of formula—

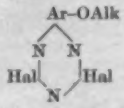


which yields an orange vat which dyes cotton pink of good fastness. C. O. C.

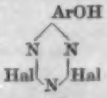
Triazine Vat Dyes and Intermediates therefor. American Cyanamid Co. *USP* 2,691,018

The nuclear OH group of hydroxy triazines are readily replaced by chlorine by treating with thionyl chloride in an inert organic solvent. The reaction can be greatly accelerated by using PCl_5 as a catalyst. *USP* 2,691,019

Compounds of formula—



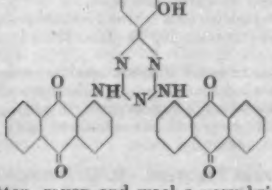
(Alk of < 6 C) when treated with a hydrogen halide of mol. wt. > 20, e.g. HCl, are dealkylated to yield compounds of formula—



which may be condensed with anthraquinonylamines to yield vat dyes which are brighter than similar dyes in which there is no substitution of hydroxyl in the 2-acyl group. *USP* 2,691,020

Dyes of the type mentioned above are obtained by making a compound of formula—

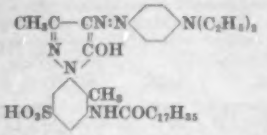
(Ar = *o*-arylene; Alk of < 6C; Aq = *a*-anthraquinonyl) and then dealkylating it with a hydrogen halide. Thus a stirring of acetone (120) and dicyandiamide (21) cooled to 5–10°c. is treated with KOH (26·4). After stirring at 0–5°c. until the reaction is complete the mixture is cooled to < 0°c. and *o*-methoxybenzoyl chloride (34·1) in acetone (120) added and stirring continued until the mixture reaches room temperature. It is then diluted with water (1000) and acetic acid (14) slowly added. The resulting *o*-methoxybenzoyldicyandiamide is filtered off, washed and air dried. This product (80), water (400), and conc. HCl are refluxed until biuret formation is complete, cooled, filtered, washed with very dil. HCl and air dried. The *o*-methoxybenzoylbiuret (10) is refluxed with PCl_5 (21) and $POCl_3$ (46) until chlorination is complete. The mixture is rapidly drowned in ice water (800), filtered, washed and dried. The resulting 2-*o*-methoxyphenyldichlorotriazine (128), *a*-aminoanthraquinone (223) and nitrobenzene (1200) are heated at 120°c. until condensation is completed after which it is cooled and filtered. A slurry of the product (30) in nitrobenzene (300) is heated to 135°c. and dry HCl gas passed through for a few minutes at intervals while the mixture is gradually brought to 200°c. The mixture is then cooled, the product filtered off, washed with nitrobenzene and alcohol, and dried at 60°c. It has the formula—



and dyes cotton, rayon and wool a very bright greenish yellow of excellent fastness. C. O. C.

Azo Pyrazolones Bleachable in Ferricyanide Compositions. General Aniline. *USP* 2,687,957

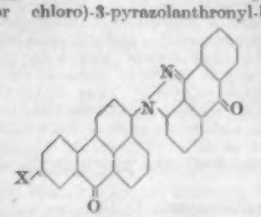
Any non-diffusing azo pyrazolone in which the aromatic radical joined to the pyrazolone by the azo group contains at least one potent electro-positive substituent in the molecule, preferably in the *para*-position of the aromatic nucleus, e.g.



are very useful as filter and antihalation dyes in colour photography. They are readily bleached in the usual ferricyanide bleach composition. C. O. C.

Pyrazolanthronyl-Benzanthrone Vat Dyes. American Cyanamid. *USP* 2,673,851

9-Bromo-(or chloro)-3-pyrazolanthronyl-benzanthrone



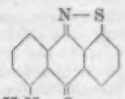
(X = Cl or Br) is heated with KOH in methanol at 140–145°c. until the halogen is eliminated. The product, separated by diluting with water and aerating, is a green navy blue vat dye. R. K. F.

1-*N*-Benzanthronyl-Aminoanthraquinones— Pigments. S. *BP* 733,461

The 1-*N*-(3-benzanthronyl)-aminoanthraquinones of *BP* 603,495 (J.S.D.C., **64**, 371 (Nov. 1948)) are, after acid pasting, or grinding preferably in presence of a water-soluble inorganic salt, pigments suitable for printing or spin-dyeing textiles, or colouring plastics or paper. Thus, 1-*N*-(3-benzanthronyl)-aminoanthraquinone, obtained by condensing 3-bromobenzanthrone with 1-aminoanthraquinone is dissolved in H_2SO_4. The solution is run in a thin stream into water. R. K. F.

***iso*Thiazolanthrone Derivatives— Pigments.** S. *BP* 733,460

5-Amino-1:9-*iso*thiazolanthrone



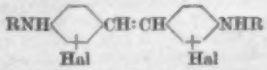
is condensed with a halogeno-benzanthrone or anthraquinone to give products

y–R–z

(R = benzanthrone or anthraquinone residue; y = 1:9-*iso*thiazolanthronyl-5-imino; z = H or y) which after acid pasting and/or grinding, is a pigment suitable for the printing or spin-dyeing of textiles, or the colouring of plastics or paper. Thus 5-amino-1:9-*iso*thiazolanthrone, 1-chloroanthraquinone, Na_2CO_3 and $CuSO_4$ are heated at 180–210°c. in nitrobenzene until condensation is complete. After filtering and washing with ethanol the product is sulphuric acid pasted to give a red pigment. R. K. F.

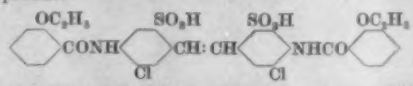
Sulphonated Dihalogenodiaminostilbenes— Fluorescent Brightening Agents. American Cyanamid Co. *USP* 2,688,617

Compounds of formula—



(R = acyl attached to the N atom by a carbon to nitrogen bond) when sulphonated in the stilbene and/or the R groups are fluorescent brightening agents resistant to hypochlorite and free from any tendency to discolour either detergents or fabrics. Thus 5:5′-dichloro-4:4′-diaminostilbene-2:2′-disulphonic acid (15 parts) and dry pyridine (735) are stirred and refluxed and gradually treated with *o*-ethoxybenzoyl chloride (37·6). Stirring and refluxing continue until no free primary amino groups are present.

The mixture is then drowned in water (700) together with enough Na_2CO_3 to render the mixture weakly alkaline. Salt (20) is added and the solution steam distilled to remove the pyridine. The resulting slurry is filtered at room temperature, washed with 2% brine and dried at 100°C. The product



has good affinity for cotton to which it imparts bluish fluorescence. C. O. C.

Blue Sulphur Dye. DuP. *USP* 2,676,171

The blue sulphur dye produced by thionating a mixture of the indophenols formed by condensing *p*-nitrosophenol with diphenylamine and diphenylamine-4-sulphonic acid respectively, is more soluble and exhausts better than the mixture of the dyes formed separately from the two indophenols; and is therefore suitable for applying in machine and package dyeing. Thus, diphenylamine *leuco*-indophenol and diphenylamine-4-sulphonic acid *leuco*-indophenol are added to a melt of Na_2S and S in "Cellosolve", heated at 107–110°C. for 72 hr., diluted, made alkaline and aerated. The dye is finally separated by adding NaCl. R. K. F.

Copper Phthalocyanine. DuP. *USP* 2,668,171

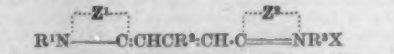
In the "urea-solvent" process for copper phthalocyanine, separation is effected by extracting the reaction mass with aq. alkali metal hydroxide, steam distilling off the solvent and finally filtering. Thus all parts being by weight the reaction product of phthalic anhydride (100), $CuCl_2$ (23) urea (147), ammonium molybdate (0·25) and trichlorobenzene (362) was poured into NaOH (35) in water (370). After heating to 100°C. with live steam the aq. layer was separated; water (290) added, heated and re-decanted three times. The solvent was next removed by steam distillation— no foaming occurs— and the pigment filtered off. R. K. F.

Phthalocyanine Process. General Aniline. *USP* 2,673,854

Yields of phthalocyanines of metals other than copper and copper hexadecachlorophthalocyanine, when made by the "urea-solvent" process, are improved by including in the reaction mixture < 25% of the weight of the phthalocyanine intermediate of a sulphate, a sulphuric ester (1–5 C) or sulphamic acid. Thus, all parts being by weight, phthalic anhydride (10·5), urea (12·5), ammonium molybdate (0·25) and Na_2SO_4 (5·4) are stirred with trichlorobenzene (35). $AlCl_3$ (3) in trichlorobenzene (5) is added and the whole refluxed at 200–205°C. for 6 hr. Urea (5·4) in trichlorobenzene (10) is introduced and refluxing continued for 5 hr. An 85% yield of aluminium phthalocyanine is obtained compared with about 12% if the Na_2SO_4 is omitted. R. K. F.

Benziminazolocarbocyanine Dyes. Eastman Kodak Co. *USP* 2,688,545

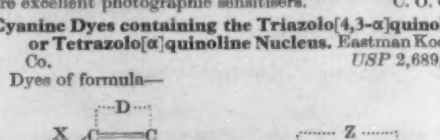
Dyes of formula—



(R^1 and R^2 = same or different Alk; R^3 = Alk, Ar or a pyrryl group; X = acid radical; Z^1 and Z^2 = same or different atoms to complete a 5- or 6-membered ring), e.g. 5:5′-dichloro-3:3′:9-triethylthiocarbocyanine bromide, are excellent photographic sensitisers. C. O. C.

Cyanine Dyes containing the Triazolo[4,3-α]quinoline or Tetrazolo[α]quinoline Nucleus. Eastman Kodak Co. *USP* 2,689,849

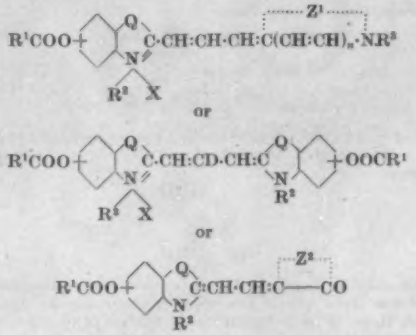
Dyes of formula—



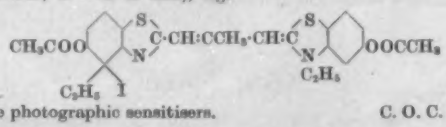
(R^1 and R^2 = same or different Alk; D = atoms to complete a carbocyclic nucleus of the benzene series; X = acid radical; Q = N or methin; *d* and *n* each = 0 or 1; Z = atoms to complete a 5- or 6-membered heterocyclic nucleus), e.g. 1′:3-diethyl-5-*s*-triazolo[4,3-α]-quino-2′-cyanine perchlorate, have good photosensitising properties. C. O. C.

Acyloxy Polymethin Dyes. Eastman Kodak Co. *USP* 2,691,652

Dyes of formula—



(R^1 = Alk; R^2 = Alk; R^3 = Ar; X = anion; Q = O or S; *n* = 0 or 1; Z^1 and Z^2 = atoms to complete a heterocyclic nucleus; D = H or Alk), e.g.—



are photographic sensitisers. C. O. C.

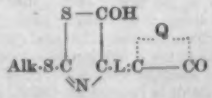
Photographic Sensitising Dyes. Kodak. *BP* 733,731

Dyes of formula—

(R = subst. or unsubst. Alk; L = subst. or unsubst. methin; *d* = 0, 1 or 2; *n* = 0 or 1; Z and Q = atoms to complete 5- or 6-membered heterocyclic nuclei), e.g. 5-[(3-ethyl-2-benzoxazolylidene)ethylidene]-3-*n*-heptyl-1-phenyl-2-thiohydantoin, are non-migrating photographic sensitisers. C. O. C.

Oxonol Dyes. Eastman Kodak Co. *USP* 2,691,581

Dyes of formula—



(L = methin which may be substituted by Alk; Q = atoms to complete a 5- or 6-membered heterocyclic nucleus), e.g. bis-4-(2-ethylthio-5(4)-thiazolone)methin oxonol, have almost as good sensitising power as merocyanine dyes. C. O. C.

Carbon Black. Godfrey L. Cabot. *BP* 733,735

A method which gives a better yield than that described in *BP* 699,406 (*J.S.D.C.*, **70**, 30 (Jan. 1955)).

USP 2,690,960

Carbon black of many different and improved properties can be produced by passing a detonation wave through a suitable hydrocarbon, e.g. acetylene, in gaseous, vapour or mist form. High yields are obtained and there is an extremely short reaction time. C. O. C.

Black Cupreous Pigment. H. H. Robertson Co. *USP* 2,690,399

A black amorphous pigment suitable for use in anti-fouling paints consists of 40–50% by wt. of metallic copper particles coated with cuprous oxide, 15–30% of cuprous oxide particles and 5–50% of cupric oxide particles. It is obtained by treating the cement or precipitated copper sludge obtained in copper refining with an alkaline

solution, preferably ammonia. The copper particles are then air oxidised and when they are the desired colour they are flash dried and ground.

USP 2,690,400

The "cement copper" is first made into an aqueous slurry, then mixed with an aqueous slurry of sulphur and the whole mass slightly acidified and boiled for 20–30 min. As soon as the free sulphur is exhausted the cuprous sulphide is allowed to settle out and the unreacted copper drawn off. C. O. C.

Titanium Dioxide. DuP. *USP* 2,689,781

High quality rutile containing a little Al_2O_3 is obtained by treating vaporised $TiCl_4$ and Al at 800–1400°C. in a closed system with a gas containing O and giving the resulting TiO_2 a pigment-finishing treatment. The product is soft and readily ground, has exceptionally high hiding power and tinting strength, is readily employed in all types of coating compositions and is especially suitable for use in coating compositions which have to be baked.

USP 2,691,571

A continuous method for air oxidising gaseous titanium tetrachloride to produce a rutile pigment. C. O. C.

Fluorescent Pigments for use in Letterpress and Screen Printing Inks. R. C. Switzer and J. L. Switzer. *BP* 733,856

A dye having fluorescent properties is dissolved or dispersed in an aqueous alkaline solution of an alkyd resin if desired in presence of a little of an organic solvent. The dyed resin is then precipitated by adding a solution, e.g. of aq. aluminium sulphate, preferably one which reacts with the excess alkali to give an insoluble dispersion. The resulting pigments are suitable for use in printing inks for application by either letterpress or screen printing methods. C. O. C.

Water-insoluble Non-swelling Organic Pigments. BASF. *BP* 734,134

Pigments having similar and in some cases better properties than those obtained by *BP* 692,654 (J.S.D.C., **69**, 307 (Aug. 1953)) are obtained by impregnating the starch or other high molecular product with a solution or suspension of an organic compound containing at least one isocyanato, ethyleneimino or quaternary ammonium group of formula—

$$Y{\cdot}CH_2NR_2X$$

(Y = acylamino or alkoxy; NR_2X = fully subst. ammonium group) or at least two ethylene oxide groups and heating the product obtained for a short time at 80–150°C. Thus maize starch is treated for 10 min. at room temperature with a 2% carbon tetrachloride solution of 1:6-hexamethylene diisocyanate and heated for 30 min. at 120°C. A flexible pigment of reduced water absorptivity and reduced swelling power is obtained. It is used as a thickener etc. for printing pastes and when coloured it is used in cosmetics. C. O. C.

Polyacetoacetyl Derivatives of Polyamines as Azo Components in Diazotype Material (IX p. 632).

V— PAINTS; ENAMELS; INKS

PATENTS

Printing Ink. J. M. Huber Corpn. *USP* 2,690,973

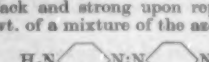
A printing ink which dries rapidly to leave a non-tacky film and which can be diluted with a large volume of water contains as the varnish an aq. solution of a lignin salt in formamide, a glycol, ester or ether of glycol. The lignin salt is obtained by neutralising one or both of the acidic groups of lignin with a nitrogenous base soluble in water to at least 5% by wt. and of dissociation constant 1×10^{-3} –1×10^{-6}. The vehicle contains 1 part of organic solvent to 2 of water. C. O. C.

Black Hectographic Ink. General Aniline. *USP* 2,691,595

Dyes of formula—

$$(H_2N)_a{-}R^1X^1Y^1{\cdot}N{:}N{-}R^2X^2Y^2$$

(a = 1 or 2; R^1 and R^2 = Ar; X^1 and Y^1 = same or different, H, Hal, Alk or alkoxy; X^2 and Y^2 = same or different, H, Alk, alkoxy, carboxy or Nab (a and b = H, Alk, hydroxyalkyl or acidyl) are mixed with black shading dyes, and the mixture blended with soluble dye salts which combine to produce a black. The resulting inks remain black and strong upon repeated use. Thus 3–1 parts by wt. of a mixture of the azo dye—



(43), C.I.681 (47) and Euchrysine 2GA conc. (G) is mixed with 1 part of a blend of C.I.21 (34), C.I.681 (11), Victoria Pure Blue BGO (G) (11), C.I.788 (17) and Euchrysine 2GA conc. (G) (7). C. O. C.

Coating Compositions. Industrial Colours. *BP* 734,181

A vehicle composed of a film-forming material dispersed or dissolved either in water or a volatile solvent has dispersed in it fine particles of a spray-dried synthetic resin or cellulose derivative which is neither soluble nor swellable in the water or solvent used. Preferably the resin or cellulose derivative has been dyed. C. O. C.

Fluorescent Pigments for use in Letterpress and Screen Printing Inks (IV this page).

VI— FIBRES; YARNS; FABRICS

Diffusion of Water Vapour through Laminae with particular reference to Textile Fabrics. M. E. Whelan, L. E. MacHattie, A. C. Goodings, and L. H. Turl. *Text. Research J.*, **25**, 197–223 (March 1955).

The transfer of moisture from the skin through clothing is important under any atmospheric conditions. Impedance to vapour movement offered by clothing will decrease the efficiency of body temperature regulation by evaporation of perspiration. In cold humid climates, where clothing which impedes vapour flow is necessary for thermal insulation, condensation may impair the insulation and cause cooling. The report, which is divided into three parts, describes work carried out since the literature review by Newnes, published in 1950, which describes investigations to this date. Part I deals with the method of measurement and includes results and discussion on the resistance to water vapour diffusion of external air layers associated with laminar materials. It is shown quantitatively that the resistance of these layers is reduced by air movement. Part II deals with the results of a study of the transmission of water vapour by diffusion through perforated metal plates and mathematical consideration of the problem. Part III deals with the resistance to diffusion of water vapour of a wide range of fabrics. A linear but non-proportional relationship between resistance and thickness is shown, and the influence of fabric construction is indicated. It is concluded from experiments on the water vapour permeability of layers of impermeable particles and films that, except in the case of very dense fabrics at very high humidity, transmission of water vapour by the fibre does not contribute appreciably to the diffusion resistance of the fabric as a whole. W. P. M.

Entropy Changes accompanying the Stretching of Cellulose Fibres in Water. G. M. Bryant and H. Wakeham. *Text. Research J.*, **25**, 224–235 (March 1955).

Force–temperature behaviour of cellulosic fibres in water is related to the entropy of stretching thermodynamically. Force–temperature measurements can be used to classify the elastic behaviour of fibres in water as either glass-like or rubber-like; but experimental data on the sorption and swelling of cellulose in water are insufficient to enable the influence of water–fibre interactions, on the observed behaviour, to be determined. A transition in the elasticity of viscose rayon, from glass-like to rubber-like, occurs at 45°c., and alkali swelling of viscose rayon causes an increase in rubber-like elasticity and a lowering of the transition temperature. The elasticity of cotton is primarily due to energy forces, and mercerisation causes no marked change in behaviour between 0° and 80°c. Comparison of highly oriented cellulose acetate before and after saponification shows that the acetate side-groups cause the temperature of transition to rubber-like elasticity to be lower, owing to a reduction in intermolecular attractions and restrictions on chain motion. Commercial-type cellulose acetate fibres at low extensions exhibit

glass-like elasticity while at high extensions the transition temperature decreases with increasing stretch. This indicates complex structural changes in the fibre as it is being stretched. W. P. M.

Effect of the Distribution of Methoxyl Groups upon some Textile Properties of Methylated Cotton Fibre. R. E. Reeves, A. C. Armstrong, F. A. Blonin, and L. W. Mazzeno. *Text. Research J.*, **25**, 257–261 (March 1955).

The methylation of cotton by (*a*) dimethyl sulphate and (*b*) diazomethane, and the investigation of the differing properties of the products and the distribution of the substituents in them, is described. The products resulting from methylation with diazomethane retained their original wet and dry strength, had greatly increased rot resistance and were not appreciably stiffened, whereas methyl celluloses, having the same degree of substitution, resulting from methylation with dimethyl sulphate, had greatly reduced wet strength, no appreciable rot resistance, and were appreciably stiffened. The distribution of the substituents was determined by drastic and partial hydrolysis followed by fermention of the hydrolysates in each case and it was concluded that the method of methylation did not greatly influence the amount of unsubstituted glucose at any particular degree of substitution; but in the diazomethane methylated cottons the substituents are more concentrated in the regions of the fibre more accessible to acid hydrolysis. It is suggested that diazomethane methylation produces a concentration of substituents in the accessible regions of the fibre where substituents are most effective in conferring rot resistance, whereas dimethyl sulphate leaves many unmodified glucose units in these regions. Further, the stiffness and lower wet strength of the dimethyl sulphate products result from a greater disorganisation of the original crystallite structure. Thus to attain desirable properties, substitution in the range 0·25–1·0 per glucose unit should be carried out under conditions of minimum swelling. W. P. M.

Formation of Regenerated-cellulose Filaments from Viscose. H. Klare and A. Gröbe. *Faserforsch. und Textiltech.*, **6**, 97–105 (March 1955).

The formation of a filament from viscose is observed under the microscope, and the diameter is measured at various distances from the single-orifice spinneret. The mass velocity of the viscose supplied to the orifice (diameter varied from 60 μ. to 100 μ.) is maintained const., and the linear velocity at which the filament is drawn off is varied (*s*, the ratio of this velocity to the linear velocity at the orifice, is varied from $\sim 0{\cdot}3$ to $\sim 2{\cdot}9$). The ratio *a* of the ultimate cross-sectional area of the filament (attained at < 40 cm. from the orifice) to the area of the orifice *A* falls as *s* is increased by increasing the size of orifice or the rate of drawing off (for a given *s*, *a* increases slightly as *A* diminishes, i.e. as the extrusion velocity rises), but when *s* is sufficiently great *a* is only slightly dependent on it, the relationship being hyperbolic ($as = k$). The value of *k* depends greatly on the composition of the spinning bath (being e.g. 0·63 and 0·96 for sulphuric acid baths containing 125 g. and 600 g. of H_2SO_4, respectively), and it is regarded as an index of the state of swelling of the filament in the spinning bath. A. E. S.

Effects due to the Oxidisability of Oil-containing Materials used in the Preparatory Treatments of Rayon Yarns and Fabrics. I— The Problem; Autoxidation of Unsaturated Fats. II— Analytical Methods. K. Täufel, R. Vogel, and A. Wicklein. *Faserforsch. und Textiltech.*, **6**, 53–57 (Feb.), 114–122 (March 1955).

Recovery of Wool from Sheepskin Pieces. G. H. Green. *J. Appl. Chem.*, **5**, 296–313 (July 1955).

The methods used for the recovery of wool from sheepskin pieces are reviewed, and the digestion of skin pieces in warm water (i.e. by bacteria) and with various enzymes is investigated on the laboratory scale, the wool obtained being examined for damage (microscopical examination of fibres mounted in aq. Methylene Blue) and handle. Satisfactory preshrinkage of the skin is essential for rapid digestion, suitable treatment being immersion in water at > 70°c. for 30 min. The corium is more readily digested than the grain, and under suitable conditions the grain can be recovered almost intact. Warm-water digestion can be effected in 4 days at 37°c. without damage to the wool; no pH control is necessary, but the presence of mineral salts is necessary for rapid digestion. The process can be accelerated and the highly objectionable odour associated with bacterial action can be avoided by the use of enzyme preparations, but the temp., and sometimes pH, of the process must be carefully controlled; under proper conditions there is no damage to the wool. The mould and bacterial proteases examined act most satisfactorily at 37–40°c. and do not require pH control; some bacterial activity normally develops and is found to be essential for complete digestion. Papain acts best at pH 8 and ~ 50°c.; a 0·1% soln. digests skin completely in 24 hr. under these conditions without damage to the wool, but with rise of temp. and pH damage becomes severe. A. E. S.

Structure of Resistant Membranes isolated from Oxidised Wool. R. D. B. Fraser and G. E. Rogers. *Text. Research J.*, **25**, 235–241 (March 1955).

Evidence is presented of the nature of the resistant residue obtained from wool oxidised with peracetic acid and extracted with ammonia. The preparation of the specimens is described. The use of gold shadowing and phase contrast in optical microscopy reveals cortical cell membranes, nuclear membranes, nuclear remnants and resistant fibrils derived from the cortex, and the composite nature of the cuticular sheath. There are 17 illustrations of photomicrographs. W. P. M.

Silk Fibroin as a Fibrous Protein. F. O. Howitt. *Text. Research J.*, **25**, 242–246 (March 1955).

Silk fibroin is a simple protein free from sulphur containing amino acid residues and from amide nitrogen. The average molecular weight of soluble fibroin, as determined by ultracentrifugal and diffusion methods, is 84,000. Molecular weight determinations of the nature, proportion, and distribution of amino acids in fibroin lead to the conclusion that the number of amino acid residues in the molecule is slightly above 1000, the protein chain consisting, for the most part, of glycine and alanine residues interspaced with serine and possibly other amino acid residues with a minimum repeating unit of –glycyl–x_1–alanylglycyl–x_2– where x_1 and x_2 represent any amino acid except glycine or alanine. It is also probable that the amino acid residues with bulky side chains such as tyrosine, are grouped together in regions that are widely separated along the protein chain. These long chains form antiparallel pleats in accordance with the structural theories of Pauling and Corey. The silk filament consists of a very large number of protein chains, arranged side by side so as to form crystalline regions in which the neighbouring chains are linked principally by hydrogen bonding, and of amorphous regions where the amino acid residues with bulky side chains create disalignment, or where the alignment of the alanylglycyl units is incomplete.

Denaturation of the insoluble protein, i.e. to the form in which it occurs in the silk gland, is due to a macrofolding of the sheets of polypeptide chains so that the groups conferring hydrophilic properties on the molecule are mainly presented to the outside, a mechanism by which a globular protein can be unfolded and, by virtue of an extensive hydrogen bonding, can assume an insoluble form. W. P. M.

Experimental Studies of the Structure of Polyamide Fibres. K. Schwertassek. *Faserforsch. und Textiltech.*, **6**, 45–53 (Feb. 1955).

When various 6-nylon fibres are heated with exclusion of air, shrinkage effects, which begin at 140–160°c., are followed at t_0 (209–221°c.) by rapid shrinkage, coiling, and surface wrinkling, and then at t_s (216–230°c.) by complete melting. Microscopical observation indicates that t_0 is the m.p. of the core, and t_s the m.p. of the skin (see J.S.D.C., 71, 160 (March 1955)). The differing m.p. of core and skin may partly explain variations in m.p. cited in the literature. Broken and cut ends and crushed places in the fibre give increased iodine absorption, which are associated with changes in core structure and are independent of the presence or absence of skin (cf. J.S.D.C., 69, 228 (1953)), but the iodine absorption, unlike that of cut or crushed places in cellulose fibres, does not revert to normal when the fibre is wet and then dried, annealing of the fibre at a temp. approaching its m.p. being required to produce this effect. When a dry 6- or 6,6-nylon fibre is broken, a

thickened end is produced. A wet fibre, however, gives a sharp break, and the skin (which evidently yields before the core) and core frequently break in different places, so that there is a length of exposed core at the fibre end. In both cases the enhanced iodine absorption extends appreciably along the length of the fibre. When a viscose fibre is similarly broken under tension, the broken ends are not deformed and show no enhanced iodine absorption—it is considered that, at break, the structural elements of viscose rayon slip over one another and few adsorption-active groups are released, whereas nylon fibres have a highly "matted" structure, so that rupture is accompanied by far-reaching breakdown of structure in the neighbourhood of the break. A. E. S.

Comparison of Trelon Mixed-polyamide Fibres with Fibres derived from Simple Polyamides and Polyesters. H. Ludewig. *Faserforsch. und Textiltech.*, **6**, 277–286 (June 1955).

The manufacture and properties of Trelon polyamide fibres (see J.S.D.C., **70**, 25, 299 (1954)) are discussed very fully, and detailed comparisons are made with 6,6-nylon, 6-nylon (Perlon), 6,10-nylon, 11-nylon (Rilsan), and polyethylene terephthalate (Lanon). The Eftrelon now on the market is prepared from a mixture of 90 parts of hexamethylenediamine adipate and 10 parts of 6-hexanolactam; the marketing of 85/15 and 80/20 polymers is projected. The Wetrelon that is to be marketed is prepared from a mixture of 57 parts of hexamethylenediamine terephthalate and 43 parts of 6-hexanolactam. 90/10 Eftrelon is very similar in properties to 6,6- and 6-nylons and is intended for application primarily in continuous-filament form. Wetrelons have some wool characteristics, and the 57/43 polymer is in some respects comparable to polyethylene terephthalate fibre. The m.p.–composition curve for the Eftrelons forms a smooth festoon between the extreme points (6,6- and 6-nylons). Polymers in the neighbourhood of the minimum melt in boiling water and are sol. in hot methanol, but the 90/10 polymer is approx. equivalent to 6,6- and 6-nylons in its resistance to reagents, its moisture-regain, swelling, and shrinkage characteristics, its affinity for dyes, and its tensile properties; its m.p. is intermediate (237°C.). The corresponding Wetrelon curve consists of two steeply sloping straight lines, which intersect to form a sharp (only slightly rounded) minimum. Polymers in the neighbourhood of the minimum are plastic in hot water and sol. in hot methanol, but the 57/43 polymer (m.p. 245°C.) is very similar to 90/10 Eftrelon in the properties enumerated above, apart from shrinkage during wet treatment, which is greater both in the untreated and in the heat-set fibres. 90/10 Eftrelon is to be preferred to 6-nylon in that it has a higher m.p. (237°C. instead of 215°C.) and contains very little material of low molecular weight (aq. extract 2% instead of 10%); furthermore, it is considered that the eventual raw-material position will favour the mixed polyamide. 90/10 Eftrelon is to be preferred to 6,6-nylon in that its melt is more stable to long or strong heating and is not so sensitive to oxygen; like 6-nylon, it can be readily produced by the V.K. (simplified continuous) process, which is not suitable for the production of 6,6-nylon. 57/43 Wetrelon has several advantages over polyethylene terephthalate—less than half the amount of terephthalic acid is required for the production of a given amount of fibre; it has a lower sp. gr. (1·17 instead of 1·38); its moisture regain is higher (5% instead of 0·5%), it swells much more in water, and it is much more readily dyed; and it is more resistant to flexing and rubbing. Tests are given for the rapid differentiation of the Trelons, 6,6- and 6-nylons, and polyethylene terephthalate; they are based on observations of the behaviour of the fibres in 4·3 N-HCl. A. E. S.

Structure of Macromolecular Substances. IX—Mechanism of the Interaction between Polyamide Fibres and Phenols. V. D. Tetyushkina, A. B. Pakshver, and S. S. Frolov. *Kolloid. zhur.*, **17**, 63–67 (1955). **X—Diffusion of Phenol in Polyamide Films and Fibres.** E. K. Mankash and A. B. Pakshver. *Ibid.*, **16**, 451–454 (1954): *Chem. Abs.*, **49**, 7930 (25 June 1955).

Further studies of the diffusion of phenols in 6-nylon are described (see J.S.D.C., **70**, 31, 316 (1954)). When sorbed by the fibre, phenol, resorcinol, and salicylic acid are hydrogen-bonded to amide NH groups; salicylic acid is attached also at terminal NH_2 groups. The diffusion coeff. of phenol is highly temp.-dependent, indicating that the fibre structure becomes more open as the temp. rises. The effect of various mechanical and physical pretreatments on diffusion in 6-nylon fibres and films is determined. A. E. S.

Synthetic Fibres having "Profiled" Cross-sections. H. Böhringer and F. Bolland. *Faserforsch. und Textiltech.*, **6**, 199–203 (May 1955): *Melliand Textilber.*, **36**, 677–680 (July 1955).

By the use of spinneret orifices of suitable form, polyamide and polyester fibres of serrated cross-section are prepared. Fabrics prepared from such fibres are free from defects, such as pilling, that are attributable to surface smoothness. A. E. S.

Density of Amorphous Polyethylene Terephthalate. A. B. Thompson and D. W. Woods. *Nature*, **176**, 78–79 (9 July 1955).

Infrared-absorption and density estimates of the degree of crystallinity of polyethylene terephthalate are not in agreement. It is suggested that the amorphous regions decrease in density with increasing degree of crystallinity and that voids appear in filaments. W. R. M.

Acrylic Fibres. IV—Fibres from Copolymers derived Predominantly from Acrylonitrile. A. Hunyar, H. Reichert, and H. Fark. *Faserforsch. und Textiltech.*, **6**, 145–152 (April 1955).

In continuation of work on the production of fibres from acrylonitrile polymers and copolymers (see J.S.D.C., **70**, 165, 317, 469 (1954)), fibres are prepared from copolymers of acrylonitrile with vinyl acetate, with acrylamide, with methyl methacrylate, with methacrylonitrile, and with acrylic acid, and some of their properties are determined. Apart from methacrylonitrile, which may be present at a mole fraction of 0·3 without greatly affecting the textile properties of the fibre, the various second components greatly affect extensibility and shrinkage induced by heat; the tensile strength is affected when these are present at a mole fraction of $> 0{\cdot}05$–$0{\cdot}1$, the greatest effect being exerted by vinyl acetate, which is in accord with predictions, based on reactivity considerations, which indicate that vinyl acetate will tend to alternate with acrylonitrile units rather than to participate in block formation. A. E. S.

PATENTS

Improving the Properties of Viscose Rayon. American Cyanamid Co. *BP* 734,010

Regenerated cellulose fibres having low water absorption and low wet elongation are obtained by adding a water-soluble acrylamido resin to the viscose solution and heating the regenerated cellulose to make the resin insoluble. The resin treatment can also be used for producing crimped staple fibre and for stiffening the cellulose yarns. W. G. C.

Dispersing Delustrants in Polyamides. DuP. *USP* 2,689,839

Continuous method for dispersing delustring agents in to polyamides, the delustring agent being added as an aqueous slurry to molten partly polymerised polyamide containing 5–20% by wt. of water. C. O. C.

Crinkled Polyacrylonitrile Fibres. Textile & Chemical Research Co. *BP* 733,979

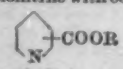
Polyacrylonitrile fibres having a very fine stable crinkle are produced by spinning a solution in dimethyl formamide of an acrylonitrile polymer having $< 85\%$ of acrylonitrile into a mixture of water, dimethyl formamide (30–60 pts.) and calcium chloride (10–30 pts.) at 15–40°C. and then washing and drying the yarn without tension. The yarns can be readily dyed and show little tendency to accumulate static electrical charges. W. G. C.

Acrylonitrile-β-Halogenoethylvinyl Ether Copolymers. Chemstrand Corpn. *USP* 2,691,645

Copolymers of 90–98% acrylonitrile and 10–2% of β-chloro(or bromo-)ethylvinyl ether are fibre forming and are readily dyed with acid dyes. C. O. C.

Acrylonitrile Polymers. Chemstrand Corpn. *USP* 2,691,641

Copolymers of acrylonitrile with compounds of formula—



(R = vinyl, allyl or methallyl) are fibre forming and have good affinity for acid dyes. C. O. C.

Acrylonitrile-Dimethylaminomethylstyrene Copolymers. DuP. *USP* 2,691,640

Copolymers of acrylonitrile and *p*-dimethylaminomethylstyrene yield fibres of high tensile strength and extraordinary durability. They have good affinity for acid dyes. C. O. C.

Ternary Acrylonitrile Polymers. American Viscose Corpn. *USP* 2,687,938

Fibres made from a copolymer of 70–98% acrylonitrile, 1–10% of a vinyl-substituted tertiary heterocyclic amine, e.g. 2-vinylpyridine, and 1–20% of vinyl acetate have good affinity for acid dyes. C. O. C.

Stable Complex Titanic Acid Esters and their Reaction with High Molecular Weight Compounds containing Hydroxyl Groups (III p. 620).

Microscopical Observations on Dyeing (VIII below).

Structure of the Tyrosine-containing Part of the Polypeptide Chain of Silk Fibroin (XII p. 635).

Kinetics and Mechanism of the Rapid Polymerisation of 6-Hexanolactam (XIII p. 635).

Kinetics of the Formation of Perlon (XIII p. 635).

Mechanical Properties of Crystalline Polymers. I— Polyamides (XIII p. 636).

Determination of the Molecular Weight Distribution Curve of Perlon by Turbidity Titration (XIV p. 638).

Microscopical Investigation of Stretch-dependent Radially Differentiated Regions in Perlon Filaments (XIV p. 638).

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Continuous Desizing of Fabrics. J. Voss. *Textil-Rund.*, **10**, 125–129 (March 1955).

The industrial availability of bacterial amylase led to the replacement of the traditional desizing process by more rapid batch-wise methods. Later, continuous processes were developed. A number of the latter are described in some detail. J. C. F.

Cleansing of Sheepskins before Dressing. W. Pense. *Rev. Tech. Ind. Cuir*, **47**, 75–80 (April), 100–104 (May 1955).

Preliminary cleansing takes place during steeping, and since detergents are seldom bacteriostatic, careful control is needed to avoid loosening of the hairs. In the subsequent scour, little use can be made of the accumulated experience of synthetic detergents in the textile industry, owing to the temp. sensitivity of the dermic substance. Skins may be permanently damaged at temp. > that of the blood of the animal (37°c.). A brief account is given of the chemical structure, and the mode of action of detergents, and useful literature references are listed. The requirements in a detergent for use with sheepskins are discussed at length, firstly those relating to general properties, and then those connected with detergent action. The effect of pH and of hard water within the permissible temp. range must be studied; detergents that are effective in the pH range 6·5–8·5 are preferred, since they do not yellow the wool. Salts— both those entering the wash liquor as impurities, and those added e.g. to assist bleaching— must not affect the action of the detergent. With very greasy fleeces, such as those in the region of the neck, a multi-stage scour with the addition of a solvent such as methylene chloride is advisable; this allows the advantageous use of different detergents at each stage. Detergents should not be used in admixture without careful consideration and prior knowledge. Experimental scours are described in which wool blends were treated with five detergents under a variety of conditions; these show the effect of temp. and of added salts. In a final discussion of the practice of scouring, the advantage of the two-bath process where the skin contains a considerable amount of impurity, is further stressed. J. W. D.

Decomposition of Sodium Chlorite in Bleach Solutions. H. Hefti. *Thesis* (E.T.H. Zürich; published by Eirene-Verlag M. Pfändler, St. Gallen. 1955), 79 pp.

A detailed review is made of literature relating to chlorine dioxide and chlorites, their effects on cellulose, their use in bleaching, and the analysis of chlorite bleach baths. An experimental study is made of the stability of chlorine dioxide and sodium chlorite in acid soln., in presence and in absence of kier-boiled cotton. Chlorine dioxide is completely stable, but sodium chlorite slowly undergoes decomposition, which proceeds in three different directions—

$$5ClO_2^- + 2H^+ = 4ClO_2 + Cl^- + 2OH^- \quad (1)$$

$$3ClO_2^- = 2ClO_3^- + Cl^- \quad (2)$$

$$ClO_2^- = Cl^- + 2O \quad (3)$$

The first reaction is always the main process, but rise in temp. and lowering of pH accelerate the second reaction to a greater extent than the first. In absence of unbleached cotton, the whole of the active oxygen formed by (3) is evolved as molecular oxygen. The rate of oxygen evolution rises as the soln. becomes more acid, passing through a max. at pH 2·4, and then falling in soln. of still lower pH. In presence of kier-boiled cotton (1) and (2) are almost unaffected, but much of the active oxygen formed by (3) is now utilised in the bleaching process, so that less oxygen is evolved. The whiteness of the bleached fabric varies with pH in the same way as the rate of (3) does, and is therefore at a max. at pH 2·4. In the course of the bleaching the cellulose undergoes no change in degree of polymerisation and carboxyl content, and no carbonyl groups are formed. A. E. S.

PATENT

Eliminating from Polyacrylonitrile Textiles the Tendency for Non-uniform Darkening on Heating. DuP. *USP* 2,689,195

The material is desized and scoured, boiled off in an aqueous solution of a low mol. wt. carboxylic acid in presence of a little of a sulphate of a long chain aliphatic alcohol, e.g. oxalic acid and sodium lauryl sulphate, and rinsed free of acid in soft water. The treated product may be heated without developing streakiness caused by non-uniform darkening. C. O. C.

Inhibiting Tarnishing of Metals by Detergents (III p. 620).

Microscopical Observations on Dyeing (VIII below).

VIII— DYEING

Microscopical Observations on Dyeing. H. E. Millson. *Amer. Dyestuff Rep.*, **44**, P417–P436 (20 June 1955).

A detailed description is given of the Microdyeoscope, a combination instrument which permits microscopic observation and photographing of dyeing and other processes taking place in a small cell. Processes studied include scouring of greasy wool, dyeing of acid and milling dyes on wool, dyeing chrome dyes and associated problems of dye precipitation, action of levelling agents, histology of processed wool, bilateral effects in wool, bronzing in cotton dyeing, acetate and vat dyeing, and dyeing Dynel with milling dyes and a carrier. There are 39 photomicrographs. J. W. B.

Major Developments in Package Dyeing. E. Caswell. *Canadian Textile J.*, **72**, 65–67 (17 June), 54–57 (1 July 1955).

A review of yarn preparation, dyes and dyeing, winding, and synthetic yarn dyeing problems. Carpet yarn, elastic nylon yarn, and Dacron blends are included in the survey. A. H.

Diffusion of Various Substances through Films of Hydrate Cellulose. A. B. Pakshver and I. V. Bŷkova. *Kolloid. zhur.*, **16**, 381–386 (1954): *Chem. Abs.*, **49**, 2821 (10 March 1955).

Diffusion data are presented for soln. of NaOH, glycerol, and Methylene Blue in contact with Cellophane film, the effect of the swelling of the film during diffusion and of drying the film under tension before use being particularly considered. A. E. S.

Pad Dyeings with Direct Dyes. K. Scheller. *Textil-Rund.*, **10**, 123–125 (March 1955).

The essential differences in physical mechanism underlying the pad dyeing of dry fabrics and the jig dyeing of

wet fabrics are explained. In pad dyeing the affinity of the dye and the speed of dyeing are of paramount importance. Pad dyeing is essentially cheaper than jig dyeing, but the process requires careful control. Fabrics must be uniformly dry, free from faults, and easily wetted. Temperature control is important because of the temperature-dependent affinity of direct dyes. Dyeings of outstanding levelness are obtainable on vegetable and regenerated cellulose fibres, and excellent tone-in-tone effects with mixture fabrics. Deeper shades require fixing in a salt bath, and the salt concn. should not exceed 5 g./litre. J. C. F.

Effect of Solvent on Dye Absorption by Cellulose Triacetate. *Dyer*, 114, 143 (22 July 1955).

Addition of 1% solvent to a disperse dyebath at 80°c. results in increased dye absorption. The increase shown is in the following order— methyl*cyclo*hexanol > methyl-*cyclo*hexanone > *cyclo*hexanone > ethyl lactate. A. H.

Calorimetric Determination of Heats of Dilution, Heats of Solution, and Heat of Dyeing on to Wool of Naphthalene Orange G. A. N. Derbyshire. *Trans. Faraday Soc.*, 51, 909–918 (July 1955).

Calorimetric measurements have been made at 25°c. of the heats of dilution of the free acid and sodium salt of Naphthalene Orange G (ICI) (sulphanilic acid→β-naphthol). The heat of solution of the dry and hydrated dye acid and the heat of dyeing on to wool have also been measured. Data on the sodium salt are well represented by an equation based on dimerisation of the anion, leading to a heat of dimerisation of — 10·48 kcal. per mole of dimer. Heats of solution to infinite dilution of dry and hydrated free acid are respectively + 3·4 and + 9·05 kcal./mole and the heat of dyeing of the free acid from an infinitely dilute solution on to wool is — 9·27 kcal./mole. Close agreement between the heat contents of hydrated solid dye acid and the dye–fibre complex and the magnitude of the heat of dimerisation of the dye anion support the hypothesis that in each case the binding energy is mainly due to non-polar van der Waals forces and the recombination of water molecules, separated against their mutual attraction by the hydrophobic surfaces of dye anions in solution. W. R. M.

Dyeing and Processing Elastic Nylon Hose. J. V. Boone. *Amer. Dyestuff Rep.*, 44, P 413–P 416 (20 June 1955).

A survey with emphasis on conditioning, preboarding, and dyeing, including a list of suitable dyes. J. W. B.

PATENTS

Cobalt Compounds for Stabilising Leuco Vat Dyes at High Temperatures. American Cyanamid Co. *USP* 2,690,952

Cobalt compounds prevent decomposition and dull dyeings when vat dyes which ordinarily cannot be used at high temperatures are used at such temperatures. Thus cotton dyed in a bath containing the halogenated indanthrone *C.I.* 1113, water (390 parts), NaOH 30°Bé. (12·5), sodium hydrosulphite (3), and 5% aq. cobaltous chloride (5) at 90°c. dyed much stronger and brighter than that dyed in a similar bath in absence of cobaltous chloride. C. O. C.

Improving the Light Fastness of Acid-dyed Cellulose Acetate by Treatment with Salicyclic Acid. DuP. *USP* 2,690,954

Addition of amino polymers to cellulose acetate enables it to be dyed with acid dyes and the light fastness of the resultant dyeings is improved if they are treated with salicylic acid. Thus acetate rayon containing 5% of dimethyl amino ethyl methacrylate when dyed reddish violet with 0·5% of sulphonated 2-anilino quinizarin has a light fastness of 2 on the A.A.T.C.C. scale. If the dyed material is treated for 5 min. in 40 times its weight of a 1·5% aqueous solution of salicylic acid then the dyeings have a light fastness of 5. C. O. C.

Dyeing Hydrophobic Textiles. Courtaulds. *BP* 724,199

Hydrophobic textiles, e.g. acetate rayon, nylon, Terylene or polyacrylonitrile fibres, are readily dyed with anionic dyes, particularly with acid or direct dyes, in a bath made by dissolving in acid a cyanamide-formaldehyde condensate and diluting the solution with water. If there is any tendency for the fastness to light of the dyeings to be reduced then a water soluble copper salt, e.g. copper acetate, may be added to the dyebath. C. O. C.

Pigmented Resin Dyeing and Printing Compositions (IX below).
Fixing Dyes and Other Organic Compounds on Fibres (IX p. 632).
Tendering of the Top Hair of Rabbitskins during Dressing and Dyeing (XIV p. 637).

IX— PRINTING

PATENTS

Photographic Stencil Screens for Half-tone Printing. Sharples Corpn. *USP* 2,690,967

The fabric of the screen is made of yarns which swell in water and have light sensitive silver salts incorporated in them during their manufacture. The fabric is impregnated with a gelatinous material free from silver salts. The fabric is then exposed and developed as usual after which it is treated with a hardening and bleaching solution which insolubilises gelatin in presence of silver. Finally it is washed with hot water to remove the remaining water-soluble gelatin. This yields a screen which yields half-tone prints of exactly the same texture as the mesh of the fabric. C. O. C.

Water-in-Lacquer Printing Emulsion. Interchemical Corpn. *USP* 2,689,162

Addition of a water-soluble silicofluoride to a pigmented water-in-lacquer emulsion containing discharging agents and a thermosetting resin as the binding agent results in prints of good colour value. The prints do not gel or lose discharge power before they are aged. C. O. C.

Pigmented Resin Dyeing and Printing Compositions. Interchemical Corpn. *USP* 2,691,005

Prints of very good fastness to rubbing are obtained by use as the printing paste of an aqueous dispersion of a water-insoluble film-forming elastomer emulsified in a pigmented lacquer. The lacquer consists of a thermo-setting resin dissolved in a volatile organic solvent in which elastomer is insoluble. Thus a 50% aq. dispersion of copolymerised ethylene dichloride and sodium poly-sulphide (Thiokol A) (24 parts) is emulsified in a lacquer made up of turpentine (57·6), 50% soln. of hydrophobic melamine-formaldehyde resin dissolved in 50/50 butanol/xylene (Melmac 245–8) (10), pine oil (3), highly ethylated ethyl cellulose (0·4), and copper phthalocyanine (6). This yields a colour concentrate which can be diluted with the above vehicle concentrate (6), mineral spirits (20 for printing paste, 40 for pad dyeing liquor), and water (74 or 54). C. O. C.

Printing Socks or the like. May Hosiery Mills. *USP* 2,690,118

Apparatus in which the dye liquor or paste, e.g. a dispersion of a vat dye or pigment, is applied to the sock or other garment by a procedure resembling screen printing. It is fully automatic, all that is required of the operator being to apply and remove the socks from the fans, the whole operation being otherwise controlled by a single foot-operated switch. C. O. C.

Multicolour Coatings. Oxford Corpn. *BP* 734,140

The design is applied to the object to be coated as a wet film and while the design is wet an inter-protecting coating of controlled incompatibility with that used for the design is applied after which the two wet films interact to effect incomplete and controlled repulsion in the wet phase. The two films are cured or set or dried simultaneously in a single operation. C. O. C.

Striped Upholstery Fabrics. United States Rubber Co. *BP* 734,257

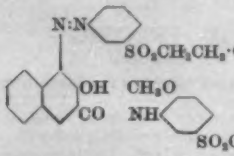
Cotton fabric of good air permeability is given a thin coating of a vinyl resin so as to provide it with a smooth surface without seriously detracting from its air permeability. A vinyl resin of a different colour from the first coating is then applied using a notched doctor so that stripes are applied to the fabric which are differently coloured from the valleys between them. This results in a fabric coated with raised stripes but which has yet good permeability to air. C. O. C.

Fixing Dyes and Other Organic Compounds on Fibres. FH. *BP* 733,471

The fibres are treated with a water-soluble derivative of a dye or other compound containing the group—

$$-SO_2\cdot CHR^1\cdot CR^2R^3\cdot OZ$$

(R^1, R^2 and R^3 = H or low mol. wt. hydrocarbon; Z = residue of a polybasic acid) and then treated with an alkaline agent to form the water-insoluble derivative of the dye or compound. Thus cotton is printed with the sodium salt of the dye—



using an aqueous paste containing the dye (3·7%), thiodiethylene glycol and tragacanth thickening. After steaming the print is treated in a bath containing 0·2% of diethylamine and 0·5% by vol. of conc. NaOH soln. A red print of very good fastness to washing and to boiling sodium carbonate soln. is obtained. Examples are given of dyeings on wool, nylon, and cotton. C. O. C.

Electrostatic Printing. Huebner Co. *USP* 2,691,343

The pigments in gaseous or liquid suspension are transferred to the fabric or paper by an electrostatic field of force. C. O. C.

Developing Diazo and Azide Sensitised Colloids. Powers Chemco. *USP* 2,690,968

A sensitised sheet of rotary photogravure tissue is formed of gelatin or a gelatinous colloid which can be selectively tanned. The photosensitive tanning agent incorporated in the sheet contains an N:N group. These agents on exposure release gaseous nitrogen and if wetted immediately after exposure the sheet would be liable to blister. This risk is obviated by subjecting the exposed sheet to suction sufficient to remove the gaseous nitrogen before placing the sheet in the developing bath. C. O. C.

Polyacetoacetyl Derivatives of Polyamines as Azo Components in Diazotype Material. General Aniline. *USP* 2,688,543

Images of excellent opacity to ultraviolet radiation and of good covering power are obtained if the polyacetoacetyl derivatives of aliphatic aromatic or heterocyclic polyamines are used as the azo components in diazotype reproductions. Used for shading in combination with such azo components as phloroglucinol or 2:3-dihydroxynaphthalene excellent neutral blacks of good opacity to ultraviolet radiation are obtained. C. O. C.

Colour Photography. P. D. Dreyfus and B. Gaspar. *USP* 2,688,542

Diazo compounds containing non-ionisable electron attracting groups such as $-NO_2$, $-CN$, $-SO_2Alk$, $-SO_2Ar$, or $-SO_2NR_2$, e.g. diazo derivatives of nitrobenzenes, phenylsulphonamides and thiazoles, produce yellow dyes with enolic or phenolic coupling components, e.g. acetoacetanilide or 2:4-dioxotetrahydroquinoline, magenta dyes with *m*-(*NN*-dialkyl)aminophenol ethers or with aryl or alkylnaphthylamines or aminonaphtholsulphonic acids, and cyan dyes with acylaminonaphthols. Thus one diazo compound can be used to react with three different coupling components each in its own layer. C. O. C.

Colour Negatives containing Masking Images for Colour Correction. General Aniline. *USP* 2,688,539

Printing Plates made by Using Aromatic *o*-Nitromethylated Compounds as Light-sensitive Substances. Kalle & Co. *BP* 733,409

Hectographic Transfer Sheet. Columbia Ribbon & Carbon Manufacturing Co. *BP* 733,472

A foundation sheet is coated with a dye carried in a waxy vehicle. It is top coated with a thin waxy layer which is sufficiently thick to prevent smudging but thin enough to allow normal pressure transfer action. C. O. C.

X—SIZING AND FINISHING

Important Variables in Textile Drying. W. H. Poole. *Canadian Textile J.*, **72**, 49–53 (3 June 1955).

The method of applying the hot air, i.e. still air, cross circulation, one side impingement, two side impingement, nozzle velocity, and nearness of nozzle to cloth, proportion of circulated air exhausted to atmosphere, type of fibre, and added finishing agents are all discussed. In addition it is stated that yarn count and cloth construction appreciably affect the drying time. A. H.

Preparation of Partly Cyanoethylated Cotton with Acrylonitrile. G. C. Daul, R. M. Reinhardt, and J. D. Reid. *Text. Research J.*, **25**, 246–253 (March 1955).

Preparation is carried out by impregnating cotton with sodium hydroxide, centrifuging and immersing in acrylonitrile under controlled conditions, the reaction being stopped by plunging into acid before rinsing and drying. Products retaining their fibrous form have been obtained with degrees of substitution up to 2·7 cyanoethyl groups per anhydroglucose unit. Maximum substitution occurs at from 10 to 15% caustic soda concentration. The rate of reaction increases with temperature especially between 60–70°C., and there is a regular rate of reaction until substitution reaches a value of 0·82 cyanoethyl groups per anhydroglucose unit after which the rate decreases. Dilution with an inert solvent (benzene) moderates the reaction but excess water decreases the amount of reaction greatly. Acrylonitrile recovered by acidifying with phosphoric acid after use, distilling and separating, contains 3% water and is satisfactory for re-use.

Hydrolysis of the cyanoethyl group occurs readily under alkaline conditions and results in both cleavage and conversion to the carboxyethyl group. With 25% sodium hydroxide solution, reacting for 16 hr., a maximum conversion of 29% of the cyanoethyl groups to carboxyethyl groups was obtained. W. P. M.

Durable Finishes for Rayon and Rayon Blends. J. A. Woodruff. *Canadian Textile J.*, **72**, 51–61 (17 June 1955).

Crease-resist finishing mixtures are given which give soft handle and shrinkage control, elimination of HCHO odour, crisp handle for glaze finishes, and simultaneous dye fixation. Abrasion resistance is discussed and a recommended application procedure for the resin described. A. H.

Rubberised Materials. V. Girtanner. *Textil-Rund.*, **10**, 105–113 (March 1955).

Rubberised materials are classified and the processes used for their manufacture outlined. Tests for water-repellency are briefly described, and the maximum permissible limits for the principal deleterious impurities in these materials (Cu, Mn, fatty matter) are discussed. Future trends include the coating of the newer synthetic fibres and the development of new coating materials. J. C. F.

PATENTS

Sighting of Textiles other than Cellulosic Textiles. Deering Milliken Research Trust. *USP* 2,690,953

Phenolic phthaleins, e.g. phenol phthalein, thymol phthalein and cresol phthalein, are very effective as sighting colours for nylon, Terylene, polyacrylonitrile fibre and their blends with wool. They are completely removed in normal scouring and in addition are completely colourless after treatment with dilute acid at room temperature. Thus the stock solution formed by dissolving barium hydroxide octahydrate (400 g.) in water (545) and adding phenol phthalein (300) and stirring until a homogeneous solution is obtained followed by adding Triton X–100 (an alkylaryl polyether wetting agent) (30) is very stable. It may be diluted to any desired extent for use as a sighting colour for nylon, etc. C. O. C.

Felted Cotton Material. Kendall Co. *USP* 2,688,864

Apparatus in which a mass of loose cotton is treated in presence of swelling agents, preferably mercerising lye, so as to cause the individual fibres to entangle, twist and felt to form a matted mass which on rinsing and drying has high flexibility, extensibility and compressibility similar to that possessed by wool felts. C. O. C.

Non-woven Fibre. International Cellucotton Products Co. *BP* 733,451

A carded lap is treated at intervals with an adhesive which becomes solid after application, the weight of adhesive used being 25–38% by wt. of the finished fabric. C. O. C.

Crease-shedding Cellulosic Cloths. Dan River Mills. *USP* 2,690,404

Use of 1 mol. of a polymethylol melamine and 2·25 mol. of dimethylol ethylene urea gives a crease-shedding finish without the finished cloth becoming yellow and losing in strength when treated with chlorine during laundering. Baking is done for 1–5 min. at 360–280°F. C. O. C.

Permanent, Lustrous, Glazed and Embossed Effects. Sayles Finishing Plants. *USP* 2,689,194

The fabric is treated with a deformable cellulosic material, then given the desired mechanical finish and finally treated with formaldehyde in presence of a catalyst and baked. If the cellulosic material is readily precipitated or regenerated then this is done at some stage during the processing of the fabric. Thus the fabric may be impregnated with aqueous cellulose xanthate, treated with acid to precipitate the cellulose, washed and while still at least slightly moist given a mechanical finish, treated with formaldehyde and ammonium thiocyanate and baked at 350°F. for a few min. Alternatively the acid treatment is not given until after the mechanical treatment or even not until after curing. C. O. C.

Resin Finish for Wool. Pacific Mills. *USP* 2,689,806

A shrink resisting finish is produced without loss in handle, tensile strength or resistance to wear, by treating wool materials with a solution or dispersion of a methylol melamine or a low alkylated methylolamine or a co-condensate of methylol melamine, e.g. with urea. When the wool is swollen the excess liquor is squeezed out and the wet material heated throughout from surface to surface uniformly and so rapidly that the resin-forming materials on the wool cannot migrate. This is done by heating the material by a high frequency electric field for 0·3–5·0 min. so that the moisture content is never $< 20\%$. C. O. C.

Reducing the Felting Power of Wool while increasing its Resistance to Abrasion. Commonwealth Scientific and Industrial Research Organisation. *USP* 2,689,193

The material is treated with caustic alkali in an organic solvent and simultaneously or subsequently with a solution of a high mol.wt. *N*-subst. linear polyamide and finally with an acid. Thus air dry wool (5 parts by wt.) was treated for 30 min. at 25°C. in ethanol (95), water (5), KOH (0·01) and *N*-subst. nylon (1·5). It was then squeezed between rollers, partly dried in air, treated for 30 min. at 25°C. in water (92·7) and HCl (7·3), rinsed and dried. In a washing test it shrank 12% in area while an untreated sample shrank 40%. The *N*-subst. nylon was obtained by heating polyhexamethylene adipamide dissolved in HCOOH with HCHO and CH_3OH until the polymer contained 10% HCHO. C. O. C.

Crinkled Yarns from Thermoplastic Filaments. Moulinage et Retorderie De Chavanoz. *BP* 733,707

Thermoplastic filaments, e.g. nylon, are passed into hot water or steam in such a way that they emerge from the medium into a false-twister, the twist so applied running back into the yarn while still in the medium. This twist is set, and, when the yarn ultimately passes to the far side of the twister, is automatically removed and leaves the yarns in a crinkled condition. J. W. B.

Pleating Cloth. Rock Hill Printing & Finishing Co. *USP* 2,689,070

The cloth is gathered widthwise from the centre and the gathers folded into pleats while it is continuously drawn lengthwise by means which apply heat and pressure to set the pleats. C. O. C.

Improving the Adhesion of Polyester Resins to Glass Fibres. Libbey-Owens-Ford Glass Co. *USP* 2,688,006

Glass fibres when treated with an aqueous solution of an alkenyl silicone ester and dried can be much more finely bonded to polyester resins. C. O. C.

Coating Glass Fabric with Butadiene-Acrylonitrile Copolymer. Owens-Corning Fiberglas Corpn. *USP* 2,686,737

The desized fabric is treated with a butadiene-acrylonitrile copolymer to which a colouring agent has been added, e.g. Hycar OR–25 or PA (B. F. Goodrich Chemical Rubber Co.) and Malachite Green, the coating dried and set. The coated fabric is then treated with a highly receptive and adherent water repellent, e.g. stearatochromyl chloride. C. O. C.

Silica Textiles. H. I. Thompson Co. *USP* 2,686,954

Glass fibres which have been leached to such an extent that the ratio of SiO_2 to other metallic oxides is $< 9{:}1$, are spun and woven and the fabric fired to dehydrate the silica. C. O. C.

Effect of the Distribution of Methoxyl Groups upon some Textile Properties of Methylated Cotton Fibre (VI p. 628).

Striped Upholstery Fabrics (IX p. 631).

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Investigation by Paper Chromatography of the Carbohydrate Composition of Hydrolysates of various Woods. R. Wittmer. *Faserforsch. und Textiltech.*, **6**, 58–62 (Feb. 1955).

Fine Structure of Cellulose and other Microfibrillar Substances. V. Balashov and R. D. Preston. *Nature*, **176**, 64–65 (9 July 1955).

Electron-diffraction diagrams of Valonia cellulose indicate that the glucose residues are so arranged that two sides of the glucose residue rings are oriented approximately parallel to the fibre axis. The thermal motion of the chains is also shown. The thickness of the crystallites in the single layer of the cell wall on alga Valonia is about 100–500 A. Comparison of this value with the width of microfibrils in the cell wall suggests that the microfibrils are almost pure crystalline solids. The observation that the microfibrils of cellulose are of the same order of diameter irrespective of their internal structure leads to the speculation that there may be something special about dimensions centring roughly around 200 A. Data for the size of other fibriform bodies is presented and attention directed to the similarity in size between the finest units visible in a number of substances of very different chemical constitution. It is suggested that there may be some principle of structure conferring special stability in fibres or sheets about 200 A. thick. W. R. M.

Structures of Different Modifications of Cellulose. D. V. Zharkovskiĭ and S. M. Lipatou. *Vestsi Akad. Navuk Belarus. S.S.R.*, (2), 160–168 (1952): *Chem. Abs.*, **49**, 3533 (10 March 1955).

Data are given for Methylene Blue absorption and heats of solvation (by water, 2% and 16% aq. NaOH, 65% aq. ethanol, and benzene) of native cellulose (I), hydrate cellulose (II, obtained from I by treatment with 18% NaOH), and disintegrated cellulose (III, obtained by grinding I in a ball mill). As a result of the mechanical rupture of the macromolecules, both polar and non-polar groups are more active in III than in I. When moistened III is heated (100–140°), recrystallisation occurs, and its structure tends to revert to that of I. The amorphous-crystalline ratios of the various cellulose samples are calculated from the heats of solvation. A. E. S.

Kinetics of Soda Cellulose Formation. B. Philipp. *Faserforsch. und Textiltech.*, **6**, 180–181 (April 1955).

Spruce sulphite cellulose (89% α-cellulose), (*a*) dried *in vacuo* at 20°C. and (*b*) dried under atmospheric pressure at 105°C., is immersed in NaOH soln., and the rate of uptake of NaOH is measured. As the NaOH concn. increases, the rate of uptake increases up to a max. value and then falls, the max. being flat and extending over the range 12–20% NaOH. The curves for (*a*) and (*b*) are similar in form, but (*a*) reacts much more rapidly than (*b*), particularly at concn. of $> 25\%$ NaOH. In accord with explanations advanced by others for similar phenomena observed in the xanthation of cellulose, it is considered that at $> 23\%$ NaOH almost the whole of the water is bound in hydration envelopes of NaOH ion-dipoles, so that very little is available for participation in reaction. A. E. S.

Constitution of Alkali-cellulose. K. Hess, K. E. Heumann, and R. Leipold. *Annalen*, 594, 119–136 (July 1955).

Repetition and investigation of the methylation of alkali-cellulose by the method of Sugihara and Wolfrom (*J. Amer. Chem. Soc.*, 71, 3509 (1949)) leads to results which differ from those obtained by these authors. An almost random distribution of methyl groups is found, not merely methylation at position 2 of the glucose residues. It is confirmed that alkalicellulose will not react with methyl iodide in the complete absence of water. From the large amounts of dimethyl- and trimethylglucose residues present it is concluded that preferential reaction at a particular hydroxyl group cannot be occurring. The necessity to have water present suggests that a definite alcoholate is not formed. The methylation of alkali-cellulose with methyl iodide in near-anhydrous conditions gives results very similar to those obtained using diazomethane in the presence of water. H. E. N.

Distribution of the Substituents in Heterogeneously Methylated Celluloses. T. Abe, K. Matsugaki, A. Hatano, and H. Sobue. *Text. Research J.*, 25, 254–256 (March 1955).

Four methylcelluloses made from cotton linters with dimethyl sulphate and alkali in toluene, so that methylation was heterogeneous, and one commercial product, were hydrolysed. Unsubstituted glucose and monomethyl-, dimethyl-, and trimethyl-glucose in the hydrolysates were separated by filter-paper chromatopile, and the results were compared with the calculated values of Spurlin and the experimental values of other workers. It was concluded that the heterogeneous methylation is initially an intermicellar reaction and then, as the degree of substitution becomes higher, the methylation takes place in the crystalline region, the reaction becomes permutoid, and the distribution of the substituents becomes identical with that calculated by Spurlin. W. P. M.

PATENT

Benzene Hexachloride as Extender for Ethyl Cellulose Plastics. Olin-Mathieson Chemical Corpn. *BP* 734,370

Benzenehexachloride is compatible with ethylcellulose to about 20%. It can be used as an extender which has little effect on the desirable properties of the ethylcellulose and which has the advantage of imparting a flame retardant property to films and mouldings made from such plastics. C. O. C.

Stable Complex Titanic Acid Esters and their Reaction with High Molecular Weight Compounds containing Hydroxyl Groups (III p. 620).

Effect of the Distribution of Methoxyl Groups upon some Textile Properties of Methylated Cotton Fibres (VI p. 628).

Reflection Measurements of Fluorescent Papers (XIV p. 637).

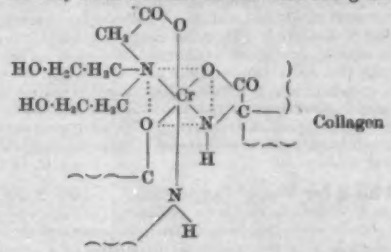
XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Unhairing of Hides and Skins by Amylase Preparations. T. C. Gordon. *J. Amer. Leather Chem. Assocn.*, 50, 270–274 (June 1955).

Enzymes do not appear to be able to penetrate to the hair roots without prior action of NaCl, urea or, perhaps, other materials. The function of these substances is, as yet, not clear, but they may dissolve some constituent of the hide which prevents the action of the enzyme. Commercial amylases are not single enzymes, and it may be that an entirely unsuspected enzyme is responsible for the depilatory action. Some reducing substance, presumably a sugar, is produced by the action of enzymes on hides, but attempts to correlate the release of this substance with the looseness of the hair have so far failed. J. W. D.

Metal-chelate Tanning Agents. A. J. Gard. *J. Amer. Leather Chem. Assocn.*, 50, 255–263 (May 1955).

The basic principles of chelate formation with hydrated Cr^{3+} ions in soln. are outlined, with particular reference to the use of amino carboxylic acids as ligands. Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand, the Cr chelate complex of which is so stable that no Cr fixation occurs with leather even though the pH is lowered to 4; the chelate contains 4 or 5 5-membered rings. Nitrilotricarboxylic acid (NTA) forms a stable, tetradentate structure, which would probably also preclude Cr fixation. β-Hydroxyethylaminodiacetic acid contains one less COOH group than NTA, and its hydroxyethyl group is virtually non-chelating; at pH 4, 4·08% Cr fixation takes place with this chelate, giving a shrinkage temp. of 196°F. With bis(hydroxyethyl)glycine, two inactive hydroxyethyl groups replace two blocking groups (acetate) on the amino group, and although a tetradentate structure is formed, four co-ordinating positions are available to the donor groups of the collagen. In this case there is 6·47% Cr fixation, and the resulting shrinkage temp. is 210°F. In the formation of this last (1 : 1) chelate, the proton is displaced from the amino group of the chelating agent, and this reacts with the OH group of $CrOHCl_2$ to form a mole of water. The hydroxyethyl groups are involved in co-ordination with the dissociation of two protons, the pH of the soln. dropping in consequence; a neutral chelate results, and this may form a double chelate with collagen—



This chelate tannage yields a more completely saturated Cr aquo ion, and thus a more stable fixation, than does the normal fixed basic Cr tannage; the alkoxide groups have a residual but limited affinity for dyes and tannins. The use of metal chelates should greatly simplify tannage, and should improve the dyeability of the leather, and the rub-resistance of the colours. J. W. D.

Colour of Dyed Leather. G. Strauss, R. Stubbings, and D. Nemes. *J. Amer. Leather Chem. Assocn.*, 50, 218–235 (May 1955).

The dye locus for a given dye is constant on various leathers, and under a variety of dyeing conditions; it is changed only if (1) the colour of the dye itself varies with pH; (2) other coloured substances are present; vegetable tannins produce duller colours; (3) the degree of aggregation of the dye is changed. Aggregation may be reduced by neutral syntans, or increased by unfavourable pH, too low a temperature, or excessively high dye levels. The constancy of the dye locus in the absence of additives, suggests that in most cases, and for usual dyeing conditions, the degree of aggregation is constant for a given dye. The colouring efficiency of a given dye varies considerably with (1) inherent colouring power, and (2) the degree of penetration— which is sensitive to minute changes in the leather and/or dyeing conditions. This depends upon the rates of diffusion and of adsorption, and the degree of aggregation. The paper begins with a detailed discussion of the numerical definition and instrumental methods of measuring surface colour. Results are quoted in terms of Hunter values. J. W. D.

Surface Areas of Collagen and Leather. R. G. Mitton and R. J. Mawhinney. *J. Soc. Leather Trades Chem.*, 39, 172–183 (June 1955).

The surface areas of hide powder (I), chrome-tanned hide powder (II), and chrome- (III) and vegetable-tanned (IV) leathers, have been determined from measurements of the adsorption of N, at the temp. of liquid N; the method is described, and there is a sketch of the apparatus. The specific surface areas of the dry samples increase in the order— II, I, III, IV, whilst those of moist samples increase with moisture content to a max. at ca. 10–12%, thereafter decreasing. The greatest overall variation occurs with II, and the smallest with IV; these increases, which are too great to be attributed to swelling alone, appear to be due to the splitting of the fibres by forces set up when a moisture gradient is produced in them. Large increases in surface area obtained when the dry leathers were degreased— 1·75 to 5·30 $m^2/g.$ with IV, and 1·18 to

1·75 m².g. with III. It is thought that grease may block the ends of existing cracks, excluding N. The effective size of the collagen fibres calc. from the surface area measurements is much larger than that of the fibrils revealed by electron microscopy, and these latter are apparently so closely packed that N cannot penetrate to their whole surfaces. J. W. D.

Molecular Organisation of Collagen. K. H. Gustavson. *J. Amer. Leather Chem. Assocn.*, **50**, 239–255 (May 1955).

The behaviour of collagens and gelatin (native and modified) towards various agents, and the nature of their titration curves, suggest that in addition to the cross-links generally recognised (H bonds and salt linkages), collagens contain two other types of stabilising cross-links. (1) In mammalian collagen (I), inter-molecular H bonding between the OH group of hydroxy-amino acid residues (mainly hydroxyproline) and the CO group of keto-imide groups on adjacent chains, is considered to be responsible for the hydrothermal stability of I in the range (40–65°C.) exceeding the shrinkage temp. of teleost collagen (II), from which it is virtually absent. (2) In both I and II, and probably in all other collagens, there appears to be an ester-like bond, probably formed between the OH group which resists acetylation, and the COOH group, yielding an –O·CO– interchain cross-link. Experimental evidence for this is discussed. This link probably forms the mainstay of the stability of collagens generally, and it has been detected in procollagen also. (3) When collagen is transformed into gelatin, both (1) and (2) are broken, and they do not, therefore, contribute much to the stability of gelatin. This conversion involves more than the breaking of H bonds and salt linkages. The third type of linkage supposed to be present in collagens as well as in ordinary non-degraded gelatins, is assumed to involve the guanidyl group, resulting in the withdrawal of the COOH group from the ionic equilibrium; further evidence of this partial masking of the arginine residue is cited. (4) The concept of interchain cross-link formation between tanning agents and collagen is reviewed, and experimental evidence for the formation is given. The same type of cross-links are probably formed between adjacent helices of collagen. The formation of intrahelical cross-links by long-chain and bulky tanning agents appears less likely for reasons of spatial accommodation. The band–interband concept of Bear (*Adv. Protein Chem.*, **7**, 69 (1952)) for the distribution of the two main types of amino acid residues in collagen is discussed, and recent supporting evidence is cited. There are 57 references to the literature. J. W. D.

Isolation and Properties of a Collagen Soluble in a Salt Solution at Neutral pH. D. S. Jackson and J. H. Fessler. *Nature*, **176**, 69–70 (9 July 1955).

A new method of isolation and preliminary ultracentrifuge, viscosity, and birefringence studies of a collagen soluble in salt solution at pH 7 are described. On standing in various buffers at temperatures between 4° and 37°C., up to 80% was precipitated giving banded fibres up to 2000 A. in diameter. With neutral salt-soluble collagen, lateral aggregation did not exceed 100 A. W. R. M.

Structure of the Tyrosine-containing Part of the Polypeptide Chain of Silk Fibroin. K. G. Ioffe. *Biokhimiya*, **19**, 495–508 (1954): *Chem. Abs.*, **49**, 2536 (25 Feb. 1955).

By the successive application of two methods based on different principles, peptides are isolated from partially hydrolysed silk fibroin, and by the application of four specially developed specific reagents the structures of 19 cpd. (16 of them peptides) are investigated. Many of the peptides are found to contain the following arrangement—AGAG–TG–AGAG–VG–AGAG–SG– (A, G, S, T, and V denote alanine, glycine, serine, tyrosine, and valine residues, respectively). It is considered that silk-fibroin chains consist mainly (50–67%) of $[AGAG–XG]_n$, in which X is an amino-acid residue other than A or G and differing in identity from one section of the chain to another.

A. E. S.

Recovery of Wool from Sheepskin Pieces (VI p. 628).
Tendering of the Top Hair of Rabbitskins during Dressing and Dyeing (XIV p. 637).

XIII— RUBBER; RESINS; PLASTICS

Mechanism of Polycondensation. V. V. Korshak. *Faserforsch. und Textiltech.*, **6**, 241–251 (June 1955).

A survey is made of the author's work on polycondensation reactions and the mechanism of polycondensation, particularly the significance of exchange and degradation reactions and of the decarboxylation of dicarboxylic acids in the preparation of polyesters and polyamides and in determining the form of their mol.wt. distribution functions. Much of this work has been abstracted previously (see e.g. J.S.D.C., **69**, 227 (1953); **70**, 595 (1954); **71**, 120 (Feb. 1955)).

This conference paper is followed by a long discussion, in which A. Matthes, W. Griehl, and O. Wichterle— who present papers on related matters (see below)— take part. These workers are not satisfied with Korshak's explanation of equilibration in the reaction melt with formation of polymers distributed over a very narrow mol.wt. band (instead of the wide scatter required by Flory's theory—see J.S.D.C., **69**, 227 (1953)). Korshak considers that such a state, the existence of which he has established experimentally in several different systems, is a consequence of the greater tendency of polymers of higher mol.wt. to undergo degradation. A. E. S.

Molecular-weight Distribution in Polycondensates. W. Griehl. *Faserforsch. und Textiltech.*, **6**, 260–268 (June 1955).

A discussion of the polydispersity of polyethylene terephthalate (see J.S.D.C., **71**, 121 (Feb. 1955)) is followed by an analysis of mol.wt.-distribution curves obtained by the turbidity-titration method previously described by the author (see J.S.D.C., **71**, 638 (Oct. 1955)). In general these are much more in accord with Flory's theory than with Korshak's (see previous abstract). Peculiarities of polymers obtained by the V.K. (simplified continuous) and alkaline-catalysis methods are discussed.

In the discussion that follows this paper V. V. Korshak states that the results of this rapid method, which is relatively new, must be treated with some caution. A. E. S.

Kinetics and Mechanism of the Rapid Polymerisation of 6-Hexanolactam. O. Wichterle. *Faserforsch. und Textiltech.*, 237–241 (June 1955).

The method developed by the author for the rapid polymerisation of 6-hexanolactam in presence of alkalis is studied under isothermal conditions at the b.p. of the lactam, the catalyst being Na_2CO_3 taken in various amounts. Reaction, which proceeds until equilibrium between monomer and polymer is attained, follows the kinetic law $\log [(M_0 - M_\infty)/(M_t - M_\infty)] = kt^2$ (M_t is the concn. of monomer at time t), and this equation will hold only if reaction is between the lactam and CO–NH linkages in the middle of the chain, which will proceed by rupture of these linkages and the interposition of monomer units. Reaction at the ends of chains would require kt^2 as the right-hand term of the equation. A. E. S.

Kinetics of the Formation of Perlon. A. Matthes. *Faserforsch. und Textiltech.*, **6**, 252–260 (June 1955).

A mathematical treatment of the "polymerisation" of 6-hexanolactam is given in which it is assumed that an extremely small amount of 6-aminohexanoic acid is formed by the action of the catalyst (water) on the lactam (the equilibrium being almost entirely on the side of the lactam), and this then reacts by regeneration of lactam, by dimerisation, and by condensation at the end of chains; also, terminal carboxyls of the resulting chains act as co-catalysts. The formulae obtained are in close accord with observation. Strictly speaking, the reaction is one of polycondensation, not "condensational polymerisation". A. E. S.

Polydispersity of Synthetic High Polymers determined from Rheological Measurements. K. Edelmann. *Faserforsch. und Textiltech.*, **6**, 269–277 (June 1955).

The rheological method of determining polydispersity described previously (see J.S.D.C., **70**, 330 (1954)) is applied to polyacrylonitrile preparations obtained in various ways, which are examined in 4% soln. In order that the results may accord with polydispersity values calculated from weight-average and number-average mol.wt., it must be

assumed that polymers prepared with the aid of different redox systems belong to different polymeric homologous series, each having a different Staudinger const. (K_m).
A. E. S.

Mechanical Properties of Crystalline Polymers. I— Polyamides. V. A. Kargin and T. I. Sogolova. *Zhur. fiz. khim.*, **27**, 1039–1049 (1953): *Chem. Abs.*, **49**, 5880 (25 April 1955).

Stress-strain curves for crystalline polyamides show that, as the polymer is stretched, its properties change discontinuously and corresponding changes in the orientation of the micro-crystals occur. The re-orientation of the crystals is discussed.
A. E. S.

Termination Reaction in Vinyl Polymerisation: Preparation of Block Polymers. C. H. Bamford and A. D. Jenkins. *Nature*, **176**, 78 (9 July 1955).

The use of initiators containing functional groups, so arranged that every free radical produced contains one such group, together with suitable coupling reactions, enables block polymers to be simply prepared.
W. R. M.

Synthesis of Polyurethans. A. A. Strepikheev, A. A. Artem'ev, and Ya. A. Shmidt. *Issledovaniya v oblasti vysokomolekul. soedinenii, Doklady 6-oi konf. vysokomolekul. soedineniyam, Akad. Nauk. S.S.S.R.*, 69–77 (1949): *Chem. Abs.*, **49**, 6122 (10 May 1955).

Hexamethylene di-*iso*cyanate is condensed with the following— $OH \cdot [CH_2]_4 \cdot OH$, $O(CH_2 \cdot CH_2 \cdot OH)_2$, $S(CH_2 \cdot CH_2 \cdot OH)_2$, $HN(CH_2 \cdot CH_2 \cdot OH)_2$, $CH_3 \cdot N(CH_2 \cdot CH_2 \cdot OH)_2$, $NH_2 \cdot [CH_2]_6 \cdot NH_2$, $NH_2 \cdot [CH_2]_6 \cdot NH_2$, $NH_2 \cdot [CH_2]_{10} \cdot NH_2$, and piperazine. The properties of the resulting polyurethans and polyureas are described.
A. E. S.

Macromolecular Compounds. XLVIII— Kinetics of the Polycondensation of 2-Aminoethanol with Sebacic Acid. G. N. Chelnokova and V. V. Korshak. *Sbornik statei obshchei khim.*, **2**, 1070–1074. **XLIX— Peculiar Features of the Reaction of 2-Aminoethanol with Adipic and Sebacic Acids.** G. N. Chelnokova, V. V. Korshak, and S. R. Rafikov. *Ibid.*, **2**, 1075–1080. **L— Mechanism of the Polycondensation of 2-Aminoethanol with Dicarboxylic Acids.** V. V. Korshak, G. N. Chelnokova, and G. I. Distler. *Ibid.*, **2**, 1278–1283 (1953): *Chem. Abs.*, **49**, 5296 (25 April 1955).

PATENTS

Polycondensates of Methylene-, Alkylidene- and Aralkylidene-Bishalogeno Carboxylic Amides. Vereinigte Glanzstoff-Fabriken.
BP 734,284, 734,287, 734,305, 734,312

Describe the formation of various condensates or co-condensates of compounds of formula—

$$Hal(CH_2)_nCO \cdot NH \cdot CHR \cdot NHCO(CH_2)_2Hal$$

(R = H, Alk or Ar; n = 1–4), e.g. methylene-bis-chloropropionamide. The products are used in making moulded products.
C. O. C.

Antistatic Agents for Synthetic Resins. Radio Corpn. of America. *USP* 2,690,407

An antistatic composition for treating synthetic resin articles consists of an incompletely hydrolysed water-insoluble polyvinyl alcohol and an amine acetate (chain of 6–18 C). Thus a solution for coating polystyrene articles consists of *iso*propanol (91% grade) (9464 c.c.), distilled water (9464 c.c.), octadecyl amine acetate (43 g.), polyvinyl alcohol (made by hydrolysing polyvinyl acetate to about 43–50%) (43 g.).
C. O. C.

Stable Complex Titanic Acid Esters and their Reaction with High Molecular Weight Compounds containing Hydroxyl Groups (III p. 620).

Rubberised Materials (X· p. 632).

Benzene Hexachloride as Extender for Ethyl Cellulose Plastics (XI p. 634).

Ultracentrifuge Investigation of the Molecular-weight Distribution of Polymers (XIV p. 638).

Molecular-weight Distribution of Polymers (XIV p. 638).

XIV— ANALYSIS; TESTING; APPARATUS

Rapid Method of Constructing Density-gradient Tubes. L. H. Tung and W. C. Taylor. *J. Polymer Sci.*, **17**, 441–442 (July 1955).

Two liquids of differing density are mixed, and the mixture is transferred to an empty tube at a constant flow rate. A nearly linear gradient is obtained, and densities can be determined to the fourth decimal place.
W. R. M.

Apparatus for the Production of Air of Controlled Humidity. B. I. Stafsing. *Svensk Papperstidning*, **58**, 392–394 (31 May 1955).

The simple apparatus described produces a flow of 0·5–1 litre/min. of air at 30–90 R.H.% over the range 30°C. to just above 100°C. No direct measurement of R.H. is required, but only the measurement of the two temperatures. Air is passed through water at a controlled temperature t_2 and then heated to the required temperature t_3. Provided that the air is saturated at t_2, the R.H. at t_3 is given by the ratio of the saturation vapour pressure of water at t_2 and t_3.
S. V. S.

Colorimetric Determination of Zirconium with Alizarin S. O. Gübeli and A. Jacob. *Helv. Chim. Acta*, **38**, 1026–1032 (June 1955).

Identification of Disperse Dyes on Nylon. J. R. Clegg. *Dyer*, **113**, 847–849 (27 May 1955).

Identification procedures involving chemical reagents and ultraviolet illumination are described for disperse dyes on nylon, and the successful tests are shown in tabulated form. Although limited in scope (soluble acetate and mixture dyes are excluded), the scheme gives a simple rapid identification for a range of disperse dyes, some of which have similar chemical characteristics.
A. H.

Photoelectric Colorimeter applied to the Regularity Measurement of Fabrics. A. Barella, C. Pujol, and J. Cegarra. *J. Textile Inst.*, **46**, P 325–P 327 (May 1955).

Relation of the Reflectance of Dyed Fabrics to Dye Concentration and the Instrumental Approach to Colour Matching. E. Atherton. *J.S.D.C.*, **71**, 389–398 (July 1955).

The factors governing the reflectance of light by a dyed fabric are discussed, and several theories relating this factor to dye concentration are noted. They may all be reduced approximately to simple reciprocal functions of reflectance. Special reference is made to a theoretical treatment, similar to that given by Kubelka and Munk, for conditions of normal illumination (such as prevail in a spectrophotometer), and the use of this theory in the prediction of matching recipes is illustrated with reference to a simple laboratory instrument.
AUTHOR

Measurement of the Extent of Delustring of Filament Fabrics. R. Jeffries. *J. Textile Inst.*, **46**, T 391–T 399 (June 1955).

Fabric lustre is measured photoelectrically by rotating a sample and obtaining a graphical representation of the cyclical variations in the intensity of the reflected light. The greater the lustre, the greater will be the differences between maximum and minimum reflectance; as delustring progressively increases, the diffuse background level of reflectance increases and the maxima decrease. Thus, lustre can be expressed in terms of the ratio of maximum to minimum, long-term variations in lamp intensity and photocell sensitivity do not affect the measurement, and a standard surface for calibration purposes is not required. Delustre of fabrics of different structure or different yarns cannot be measured; apart from this, the instrument will detect differences invisible by eye.
J. W. B.

Standard Method of Test for Water-repellency of Fabrics permeable to Air using a Bundesmann-type Apparatus. Textile Institute, Tentative Textile Standard No. 8, 1955. *J. Textile Inst.*, **46**, S 51–S 56 (June 1955).

Method of Testing Water-repellency of Cotton Fabrics permeable to Air using a Bundesmann-type Apparatus. J. Lord. *J. Textile Inst.*, **46**, s 57–s 82 (June 1955).

A detailed report is presented of interlaboratory trials on the use of the Bundesmann apparatus. J. W. B.

Some Arbitrary Aspects of Bundesmann Shower Testing. J. Lord. *J. Textile Inst.*, **46**, s 83–s 100 (June 1955).

Factors which can influence the results of Bundesmann shower tests are studied; they include the method of removing surplus water from exposed specimens, the temperature, pH, and hardness of the water used, the rate of flow and duration of the test, and the time during which specimens are exposed to the laboratory atmosphere before weighing. Causes of variation of drop weight, such as rate of flow and state of jet, are discussed. The effects of roughness in the wiper arms and of variations in the springs used in the cup assembly are studied as sources of variation in the cup assembly. It is suggested that an extra set of bezels (clamps), more suitable for thin fabrics of types commonly tested, should be available.

J. W. B.

Flammability Testing—Its Relation to the Law. C. A. Baker. *Amer. Dyestuff Rep.*, **44**, P 401–P 403 (6 June 1955).

Reflection Measurements of Fluorescent Papers. A. S. Stenius. *Svensk Papperstidning*, **58**, 395–396 (31 May 1955).

Spectral reflection curves obtained with the General Electric spectrophotometer and the Zeiss reflection meter are compared. S. V. S.

Tendering of the Top Hair of Rabbitskins during Dressing and Dyeing. R. Vrbacký and V. Vrbacká. *Československ. kožařství*, **2**, 45–46, 72–75 (1953): *Chem. Abs.*, **49**, 7277 (25 May 1955).

Tendering of the hairs is measured on a Chail apparatus for determining resistance of leather to rubbing, a special paper being used at 20 strokes per min. with a load of 1000 g. The number of broken hairs is counted. New skins showed 0–60 broken hairs. After tanning with HCHO and Al salts the mean value for different breeds varied from 7–28. The difference between maximum and minimum values was 74. The effect of the various dressing and dyeing operations was ascertained by taking a normal and a treated half of a skin. Killing has no effect except with 16 g./l. Na_2CO_3 which is not used in practice. Bleaching (5–10 g. H_2O_2 30% per litre after mordanting with 2 g. $Na_2Cr_2O_7$ per litre) is somewhat harmful, the amount of H_2O_2 should be kept as low as possible. Mordanting with $CuSO_4$, $FeSO_4$, or $K_2Cr_2O_7$ has no adverse effect except in the case of 2 g. $K_2Cr_2O_7$ and 4 ml. 60% acetic acid per litre. Dyeing brown for 4 hr. at 35°c. with oxidation dyes is not harmful at normal strengths (2·4 g. Ursol per litre) but damage begins when the dye strength reaches 16 g. per litre. Addition of 5–10 g. glucose or molasses per litre to the dyebath tends to prevent tendering of the hairs. Blacks were dyed by killing with 8 ml. 20% ammonia and 1 g. Sanopin L per litre for 2 hr. at 35°c., mordanting with 2 g. $K_2Cr_2O_7$ and 1 mol. 60% acetic acid per litre, then dyeing with 3 g. Ursol D, 2 g. Ursol DB, and 3·8 ml. 40% H_2O_2 per litre followed by three brushings with 40 g./l. aniline hydrochloride, 15 g./l. $NaClO_3$, 10 g./l. $CuSO_4$, $5H_2O$, 10 g./l. NH_4Cl and 1 g./l. Katexol at pH 3·1. The tendering ratio was 9:13 with 0–20 g./l. $CuSO_4$ and 13:20 with 40 g./l. With 15-30 g./l. $NaClO_3$ it was 7:10, with 0·5–40·0 g./l. NH_4Cl there was no tendering. At different pH (adjusted with HCl) the tendering ratio was 8:15 at 1·4, 34:13 at 3·9, 30:16 at 5·5. At lower pH deeper dyeings are obtained. Varying the amount of aniline hydrochloride from 40 to 50 g./l. resulted in a tendering ratio of 8:14. Adding 10 g./l. $K_2C_2O_7$ to the stock solution brought the pH to 3·4 but after three brushings the tendering index is 23:33. Adding 5 g./l. *p*-phenylenediamine to the stock solution lowered the tendering ratio to 10:6, brought the pH to 3·2 and yielded a much more intense black. Adding 1 g./l. of *p*-phenylenediamine is as effective as 40–50 g./l. of aniline-hydrochloride and results in better furs. Long drumming in sawdust is detrimental and good colour fastness must be attained by thorough washing and not by long drumming in sawdust.

C. O. C.

Sorption Chromatography of Polar Substances on Polyamides. V. Carelli, A. M. Liquori, and A. Melo. *Nature*, **176**, 70–71 (9 July 1955).

Polyhexamethylene adipamide powder has been used, with a Tiselius–Claesson apparatus, in the separation of xylenols, of *o*-cresol, *m*-cresol, and phenol, and of propionic, butyric, and caproic acids. In the cases of xylenols and phenols the extent of absorption increases with the separation between methyl and phenolic groups. This type of chromatography is termed sorption chromatography, similar to liquid–liquid partition chromatography, the main difference being that one of the two solvents is the amorphous part of the polymer. Possible applications are suggested. W. R. M.

Determination of Alkalinity and Total Cations in Water. B. A. Sard and J. Ungar. *Chem. and Ind.*, 699–700 (18 June 1955).

A column is prepared from the cation exchange resin "Zeo-Karb" 225, the occluded air is displaced upwards with dist. water, and after activation with HCl (2 N.), the column is rinsed with dist. water until the effluent is just alkaline to screened methyl orange (I). A 50-ml. sample of the water under test is passed slowly through, and the effluent is discarded. Two 100-ml. aliquots of the water are then passed through at the same rate, and the effluents collected separately; each is titrated with NaOH (0·020 N.), using I as indicator. The Equivalent Mineral Acidity (E.M.A.) is given by the formula—

$$\frac{AB}{V} \times \frac{1000}{0{\cdot}02}$$

where A is the titration figure (ml.) of a NaOH soln. of normality B, and V is the vol. of the aliquot; thus derived, the E.M.A. is expressed as mg. $CaCO_3$ per l. of water (i.e. p.p.m. $CaCO_3$). The total cation content, in terms of $CaCO_3$, is determined by adding the total alkalinity to I, to the E.M.A. The Na content is obtained by subtracting the total hardness, determined by the Versenate method according to Betz and Noll (*J. Amer. Water Wks. Assoc.*, **42**, 49–56 (1950)), from the total cations. The results agree closely with those obtained by orthodox methods. The development of the method is given in detail.

J. W. D.

Chromatography of Acid Anilides. A. P. De Jonge. *Rec. Trav. chim.*, **74**, 760–762 (June 1955).

The fatty acids (up to C_{10}) have been separated by the chromatography of their anilides. The R_f values are reported for each of these acids, with three immobile phases—80% methanol, 50% ethanol, and 20% propan-1-ol; cyclohexane was used as the mobile phase in every case. The fatty acid anilides have a high absorptivity at 243 mμ., and the spots can thus be detected by the procedure of Tennent *et al.* (*Anal. Chem.*, **23**, 1748 (1951)). This latter procedure has three advantages—(1) the distribution of the substance within the spot may be judged, (2) the effectiveness of the separation can be assessed, and (3) the anilide is not chemically changed, and the spectrum may be roughly determined, using the spot itself (for identification), and after the spots have been cut out, they can be eluted with ethanol and the extinction of the soln. measured (for determination). J. W. D.

Improved Histochemical Benzidine-Blue Peroxidase Method and a Note on the Composition of the Blue Reaction Product. P. Van Duijn. *Rec. Trav. chim.*, **74**, 771–778 (June 1955).

Ammonium chloride (5%) is added to the benzidine–H_2O_2 mixture. The blue crystals, prepared by adding a milk–peroxidase concentrate to this mixture, have a minimum formula of $C_{24}H_{24}N_4Cl{\cdot}2H_2O$, and are of extremely low solubility. The blue reaction product is considered to be, formally, in a state of reduction intermediate between benzidine, and the ion $(C_{12}H_{12}N_2)^+X^-$ postulated by Weis (*Chem. and Ind.*, **16**, 517 (1938)). J. W. D.

Air-permeability Method of Measuring the Fineness and Surface Area of Fibres. S. Meyer. *Faserforsch. und Textiltech.*, **6**, 129–137 (March 1955).

A description of the construction and use of a new apparatus for determining the surface area of fibre assemblies by the air-permeability method. A. E. S.

Determination of the Molecular Weight Distribution Curve of Perlon by Turbidity Titration. A. Gordijenko, W. Griehl, and H. Sieber. *Faserforsch. und Textiltech.*, **6**, 105–113 (March 1955).

The following method has been developed for the rapid determination of the mol.wt. distribution in Perlon L samples—a 0·006% soln. of the polymer in a mixture of cresol, *iso*butyl alcohol, *cyclo*hexane, and ligroin is titrated with a mixture of ligroin and 1:1:2:2-tetrachloroethane, turbidity measurements being made photoelectrically after each addition of this precipitant; the variation in turbidity is plotted, and the resulting curve is manipulated by the method of Morey and Tamblyn (*J. Appl. Phys.*, **16**, 419 (1945)), in which use is made of a calibration curve derived from solubility determinations on polymer fractions of known mol.wt., and is converted into a mass-distribution curve in which the specific viscosity of a fraction as a 0·5% soln. in *m*-cresol is taken as an index of D.P. (since the exact relation of D.P. to viscosity is not known for Perlon L). Some Perlon samples of identical mean D.P. but prepared under widely differing conditions are examined. Most of them give almost identical distribution curves, covering a wide range but having a sharp maximum. Alkali-catalysed polymers and some of the polymers prepared by the V.K. (simplified continuous) method differ in giving smooth, rounded curves.

A. E. S.

Microscopical Investigation of Stretch-dependent Radially Differentiated Regions in Perlon Filaments. O. de Riz, B. Hauptmann, and E. Schuller. *Faserforsch. und Textiltech.*, **6**, 123–129 (March 1955). *Melliand Textilber.*, **36**, 680–684 (July 1955).

Phenomena occurring when finely chopped Perlon filaments are heated with a $ZnCl_2$–I_2 soln. are observed under the microscope. Unstretched filaments swell, but retain their smooth surface, whereas stretched filaments acquire a wrinkled surface and swell more strongly laterally than unstretched filaments. Examination of the stained cut ends shows that the ratio of core to skin decreases greatly as stretch increases. Quantitative data are given for the dependence of swelling and of the proportions of core and skin on the degree of stretch.

A. E. S.

Colour Specification—Possible Revision of the C.I.E. System. W. S. Stiles. *Nature*, **176**, 95–97 (16 July 1955).

Estimation of Chlorides and Sulphates in Leather. J. Jany. *J. Amer. Leather Chem. Assocn.*, **50**, 235–238 (May 1955).

The finely ground leather is heated with a measured volume of Na_2CO_3 soln. in a Pt dish, using an electrically heated air bath. The mass is evaporated to dryness, preferably by the use of an infrared bulb, and ignited for 2 hr. at 400–450°C. The residue is transferred with washing, under prescribed conditions, to a beaker, and thence to a volumetric flask. The soln. is neutralised with a previously determined volume of acetic acid soln., made up to volume, and filtered; the method yields a clear, water-white extract. If present, Cr may be removed by boiling the soln. with Zn dust prior to transference to the volumetric flask. Conventional analyses with $AgNO_3$ and $BaCl_2$ are applied to the extract.

J. W. D.

Determination of Chromium in Leathers. J. R. Rossi. *Rev. Tech. Ind. Cuir*, **47**, 125–127 (June 1955).

The leather is digested with a 1 : 1 (vol./vol.) mixture of HNO_3 and H_2SO_4; perhydrol (110-vol. H_2O_2) is added, after the initial action, to complete the dissolution. The oxidation of Cr^{3+} to Cr^{6+} is effected by ammonium persulphate in moderately acid soln., in the presence of Ag^+ ions. The Cr^{6+} is determined by an iodometric method, the result being expressed in terms of Cr_2O_3. The method is proposed as a replacement for French Standard NF.G52–208, and results obtained by the two procedures are compared.

J. W. D.

Determination of the Minimum Value of the Specific Viscosity–Concentration Ratio for Solutions of High Polymers. F. Winkler. *Faserforsch. und Textiltech.*, **6**, 164–168 (April 1955).

A mathematical treatment of viscosity–concentration data which yields the most probable minimum value of η_{sp}/c (cf. J.S.D.C., **70**, 326 (1954); **71** (Aug. 1955)).

A. E. S.

Ultracentrifuge Investigation of the Molecular-weight Distribution of Polymers. S. E. Bresler and S. Ya. Frenkel. *Zhur. tekh. fiz.*, **23**, 1502–1520 (1953): *Chem. Abs.*, **49**, 3620 (25 March 1955).

A mathematical treatment is given of the sedimentation–diffusion method for determining the mol.wt.-distribution function of polymers, the application of which is described elsewhere (see below, and also J.S.D.C., **69**, 227 (1953); **70**, 377 (1954)).

A. E. S.

Molecular-weight Distribution of Polymers. S. E. Bresler, I. Ya. Poddubnyĭ, and S. Ya. Frenkel. *Zhur. tekh. fiz.*, **23**, 1521–1540 (1953): *Chem. Abs.*, **49**, 3620 (25 March 1955).

The mol.wt.-distribution functions of two butadiene polymers and a butadiene–styrene copolymer (Buna S) are determined by the method referred to in the previous abstract and by a method based on fractional precipitation, and the results are compared critically. The first method gives a more detailed picture of the distribution.

A. E. S.

Chemical Method for the Determination of Protein Rayons in Mixtures with Wool. E. Druce. *J. Textile Inst.*, **46**, T 512–T 520 (July 1955).

Mixtures of wool and protein rayons are analysed as follows: 0·3–0·5 g. of the sample is shaken in a 100-ml. flask frequently for 1 hr. with 35 ml. of a 3% soln. of peracetic acid and left overnight. The soln. is filtered (porosity-2 crucible), and the residue (protein rayon) transferred back to the flask with about 40 ml. of 0·1 N-NaOH; the flask is shaken well and immersed for 15 min. in a boiling water-bath, with frequent shaking and loosening of the stopper. After filtration the flask is rinsed with more 0·1 N-NaOH, rinsings being transferred to the crucible, and the residue washed successively with 20 ml. of hot water, 20 ml. of dilute acetic acid, and several lots of water. It is dried for $\frac{1}{4}$ 3 hr. at 110°C. To allow for the rayon dissolved, correction factors are—Ardil B 1·06, Ardil F 1·10, Fibrolane BX 1·11, Vicara 1·03; scoured fabrics (0·2% Lissapol N at 45–50°C.): Ardil B 1·05, Ardil F 1·05, Fibrolane BX 1·10, Vicara 1·02. Reproducibility is good. There is a useful survey of such separation problems, and also a discussion of purification of protein rayons prior to analysis.

J. W. B.

Microscopic Identification of Polyester Fibres. H. H. Bühler and H. Zahn. *Melliand Textilber.*, **36**, 542 (June 1955).

The fibre is stained with 0·5 g. Sudan Red in 20 ml. of 80% phenol for 60 sec. at room temp., rinsed quickly with water, and then given two 5-sec. washes with ethanol. The result is mounted in 50% glycerol, and observed in a light microscope at 60–270 X. Differentiation within the class is possible by this means, and a table is given.

S. R. C.

Tests for the Control of the Non-yellowing of Silk by Washing Preparations. J. Pinte, Mme. Pierret, and P. Rochas. *Bull. Inst. Text. France*, (54), 39–47 (June 1955).

The authors' object is to set up a test for assessing the suitability of household detergent preparations for washing silk articles without causing yellowing. A standard silk fabric is washed under controlled conditions. The reflectance of the washed sample is measured at four wavelengths (violet 4200 A., blue 4600 A., yellow 5750 A., and orange 6100 A.) or with four suitable filters, using the standard fabric washed in distilled water as reference sample. The combination of reflectances—

$$(Y + O) - (V + B)$$

is defined as the *coefficient of yellowing C*. This method of evaluation takes account of the possible presence of fluorescent brightening agents in the preparations under test. A series of samples of known *C* values was assessed visually by trained observers, and a practicable upper limit for *C* has been assigned.

J. C. F.

Testing Rubbing Fastness on Fibres, Yarns, and Cloths. F. Ruf. *Melliand Textilber.*, **36**, 755 (July 1955).

The Schröder apparatus is illustrated and described. S. R. C.

Fastness to Washing and Milling of Dyes and Prints. Anon. *Teintex*, **20**, 569–570 (July 1955).

The Prexa apparatus recommended by the E.C.E. for testing is illustrated and briefly discussed. S. R. C.

New Apparatus for Testing Flameproofness. Joint Fire Research Organisation. *Dyer*, **114**, 61–63 (8 July 1955).

The strip of material under test ($1\frac{1}{2}$ in. × 72 in.) is suspended from one arm of a torsion balance, and the bottom ignited. Weight loss as the fabric burns is measured by the balance, which carries a mirror reflecting a beam of light on to a moving film. Flame propagation speed v is arrived at by obtaining r (slope of linear portion of the recorded curve) and using this in the following equation—

$$v = \frac{rl}{w_1 - w_2}$$

where w_1 = initial weight of fabric, w_2 = final weight of residue, and l = length of test specimen. It is hoped to have this method adopted as the basis of a British Standard. A. H.

Examination of Surface-finished Textiles. W. Rotta and G. Scheurich. *Textil Praxis*, **10**, 586–589 (June 1955).

The present fashion for surface-treated cotton and spun rayon staple has resulted in importance being attached to testing methods. Photomicrographs taken both in incident and in transmitted light are used for this purpose. Useful results are obtained by making a negative of cellulose metallised with aluminium *in vacuo*, which results in clear photomicrographs and replaces photographing the actual material in the normal manner. Several illustrations are given. B. K.

PATENTS

Multicolour Printing Ink and Printing Plate Testing Press. W. B. Leavens. *USP* 2,681,006

Measuring Tension in Filamentary Material. ICI. *BP* 730,035

A device particularly suitable for measuring tension in threads travelling at high speeds, and without frictional errors due to guides or pulleys, comprises causing the tension to exert a turning moment on a pivoted bar. The filament passes round a guide on the bar which is held so that one of the filament directions is along the bar-pivot line. The bar is spring-loaded and the printed end moves over a scale which can be calibrated directly to give the tension. J. W. B.

Inspecting Continuous Fabrics or Webs and Recording Faults. A. Laszlo. *BP* 728,127

A spool of tape on which can be recorded markings in pencil, etc. is connected through a reduction gear to a fabric-inspection machine. Thus, as a sequence of faults is encountered they may be recorded in order and in equivalent spacing by the inspector, who uses whatever form of notation he wishes. J. W. B.

Testing the Uniformity of Dyeing Properties of Yarns. American Viscose Corpn. *USP* 2,692,419

The yarn in open warp form is collected upon a cylinder which is rotating and which moves in an axial direction for at least the width of the warp during each revolution so that the yarn is collected in a helical but non-overlapping pattern. It is fastened on the cylinder under controlled tension and then the cylinder is horizontally partly or wholly immersed in a dye liquor. It is run in the dye liquor for the desired time, the liquor run off or the cylinder raised, excess dye liquor removed from the yarn by rotating the cylinder and they are dried and examined. C. O. C.

Surface Tensiometer. A. P. R. Pochan. *BP* 733,602

The lower conical tip of a vertical capillary tube touches the surface of the test-liquid in a reservoir mounted on a vertically adjustable platform. Liquid is drawn up the tube by a syringe connected to the upper end of the tube then allowed to attain a free height under atmospheric pressure. Optical means are provided for accurate measurement of this height. G. E. K.

Determining the Free Carbon Content of Organic Finishing Materials. Western Electric Co. *USP* 2,688,532

The finish is heated so as to volatilise all organic components of the vehicle without oxidising the free carbon present or degrading organic matter to free carbon. The residue is then weighed and heated in an oxidising atmosphere until all the carbon is oxidised. The non-oxidisable pigments left are weighed, the loss in weight giving the amount of free carbon present in the finish. C. O. C.

Testing the Crease Resistance of Fabric. Celanese Corpn. of America. *BP* 733,284

A sample of the fabric is placed in a flexible container, e.g. a rubber bag, which is repeatedly caused to collapse by fluid pressure, e.g. by evacuating the air from the bag. After a definite number of collapses the fabric is examined in a suitable manner to determine the amount of residual creasing. C. O. C.

Abrasion Testing Machine. Board of Supervisors of Louisiana State University and Agricultural and Mechanical College. *USP* 2,687,641

Apparatus in which a large sample of cloth is secured to a drum which rotates against an abrading device. C. O. C.

Effects due to the Oxidisability of Oil-containing Materials used in the Preparatory Treatments of Rayon Yarns and Fabrics. I—The Problem; Autoxidation of Unsaturated Fats. II—Analytical Methods (VI p. 628).

Microscopical Observations on Dyeing (VIII p. 630).

XV—MISCELLANEOUS

Crystal Habit Modification of Inorganic Salts with Dyes. J. Whetstone. *Trans. Faraday Soc.*, **51**, 973–983 (July 1955).

The crystal habit modifying powers of dyes depend both on their anionic and cationic polar substituent groups and the nature of the substitution. Positions of polar substitution are critical in defining the habit modifying powers of the dye. Modified crystal growth is probably most influenced by adsorption of dye molecules on planes representing edges of growth layers tending to build up crystal faces. A mechanism is suggested for the dye adsorption process, depending on existence of similarities between patterns of the appropriate polar groups of the dye molecules and the ions of the crystal plane concerned. W. R. M.

Colour Anomaly, the Rayleigh Equation, and Selective Adaptation. R. L. Gregory. *Nature*, **176**, 172–173 (23 July 1955).

In tests with thirty normal and four anomalous observers matches between a monochromatic yellow field and a red + green mixture field remained true after adaptation with red and with green light. This is evidence against the existence of a special yellow receptor system in the retina, since this would be stimulated by the mono-chromatic yellow field but not by the adapting light. The observations also suggest that colour anomaly is due to abnormal spectral positions of the fundamental response curves rather than to abnormal sensitivities, or to neural leakage across receptor systems. A. J.

Antioxidant Activity of Redox Dyes. V. P. Maier and A. L. Tappel. *Nature*, **175**, 951–952 (28 May 1955).

New Methylene Blue, Malachite Green, Rosaniline, Bindschedler's Green, and Methyl Violet all inhibit the haematin-catalysed oxidation of cod-liver oil. Suggested mechanisms are formation of hemichromes between the dyes and haematin, termination of chain reactions by leuco dyes, or regeneration of α-tocopherol from an oxidation product, thus allowing the re-use of submininal amounts of vitamin E. A. J.

Books about Textiles—A Classified List of Recent Publications. Anon. *Dyer*, **114**, 115–117 (22 July 1955).

The Guilds of the City of London with special reference to The Worshipful Company of Dyers. P. E. Jones. J.S.D.C., **71**, 496–501 (Sept. 1955).

The history of the City guilds is outlined from medieval times until the present day. The craft of Dyers was mentioned in 1298, but the Dyers' Company was not incorporated until 1471, and reincorporated in 1472. Its subsequent history is traced. AUTHOR

J. F. Persoz 1805–1868. E. Justin-Mueller. *Teintex*, **20**, 469–470 (June 1955).

A further biography in a series on distinguished textile chemists and colourists. S. R. C.

Structural Effects on Colours in Glass. H. Cole. *Proc. Intern. Congr. Pure & Appl. Chem.*, **5**, 429–439 (1947) (Pub. 1953): *Chem. Abs.*, **49**, 7821 (10 June 1955).

Alkali metals can assume a covalency of 4 in glasses by accepting coordinate links from lone pairs of electrons from O in the silicate network. F and S in combination can similarly donate to an extent limited by their "solubility" in glass. This theory repudiates the artificial division of oxides into network formers, intermediates and modifiers. The theory is applied to the colour phenomena of the Se-amber-, S-pink-, Mn- and Cr-coloured glasses, effect of the B_2O_3 content on the colour of Na_2O–B_2O_3 glasses, and the effects of oxidation and reduction. C. O. C.

PATENTS

Mahogany Stainer Filler for Wood. Chadeloid Corpn. *BP* 728,701

An acid dye and a natural or synthetic resinous binder are dissolved in an organic solvent. In this solution there is then suspended a pore filler of which $\geq$ 18% by weight consists of activated carbon, the remainder of the filler consists of a pigment and/or an ordinary paint filler. The product is a surface coating for wood which has high colour stability and brilliance, has excellent sealing action against lacquers and varnishes and deposits in the pores of the wood an inert dark pigment which wipes clear of the surface of the wood to leave a brilliant finish. C. O. C.

Cold Manufacture of Ceramics. E. Braunstein. *BP* 728,707

Ceramics which can be obtained in any desired colour by simple addition of a suitable dye during their manufacture are made by mixing ZnO (38 parts by weight), MgO (48), Na silicate (10), Na borate (2), and soapstone (2) and then kneading the mixture with a solution made by mixing $ZnCl_2$ 45° Bé., $MgCl_2$ 30° Bé., NH_4Cl 10° Bé. and NaCl 5° Bé. The products are then allowed to set and dipped into a solution of Mg and Zn fluosilicates to render them impervious to water and give them vitreous hardness. The amount of solution added in kneading depends upon the procedure desired to be followed in making the end product (spray, casting, press moulding, etc.). C. O. C.

Stain Fillers. Chadeloid Corpn. *USP* 2,680,103

A dye is dissolved in a glycol ether solvent containing at least two ethers. The solution is mixed into a neutral paste containing an inert filler, a resin binder, wetting and dispersing agents and thinners. The product has very good penetrating and colouring power for wood. C. O. C.

Coating Surfaces with Dispersions of Solids in Liquids. Kwikform. *BP* 730,557

Settling out of the solids is prevented by mixing successive batches of the coating composition, circulating each in turn around a closed feeding circuit from which it is discharged on to the surface to be coated. As one batch goes around the feeding circuit the next successive batch is mixed and circulated around a mixing circuit until it can be passed to the feeding circuit. C. O. C.

Sweet and Confectionery Colouring Composition. Loft Candy Corpn. *USP* 2,686,722

The FD&C dyes can be incorporated into fatty compositions if they are first dissolved in ethyl alcohol and the solution added to a master batch which, after evaporation of the alcohol, is used for colouring working batches. This gives a homogeneously coloured product whereas adding the dyes directly would, except for the yellow, yield blotchy or specky products. C. O. C.

Staining and Filling Wood. Chadeloid Corpn. *USP* 2,691,564

A neutral filler paste consisting of shellac (which should be free from wax and resin), an alcohol solvent, a natural gum (as drying modifier) and an inert filler is coloured with a concentrated solution of a dye, the solvent for the dye being compatible with that used for the shellac. C. O. C.

Wood Stain. Chadeloid Corpn. *USP* 2,691,596

The water-insoluble coloured monovalent salts of a carboxy alkyl cellulose treated with tetrahydrofurfuryl alcohol containing about 1·0% of a strong alkali, e.g. NaOH, dissolve to yield a solution which may be diluted with methanol, toluol or xylol and used as a wood stain. C. O. C.

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with Aridye Pigment Colours
This reproduction of an actual print on delicate nylon illustrates one interesting use.
Though Cotton and Spun rayon provide by far the greatest outlet, ARIDYE pigment colours are successfully applied to almost every type of fibre, both natural and synthetic.
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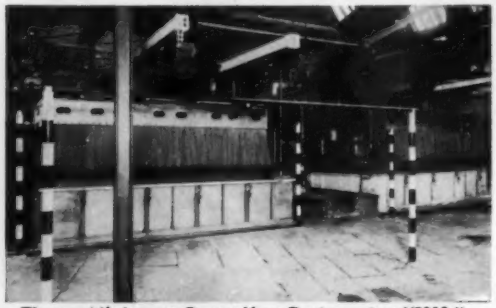
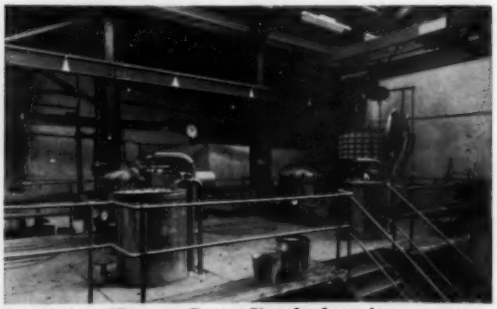
High Temperature Pressure Dyeing machine—250/300 lb. capacity

LONGCLOSE YARN DYEING PLANT



The world's largest Carpet Yarn Dyeing unit—4/5000 lb. capacity



Installation of Pressure Dyeing Plant for fast colours on cotton cheeses, cones and hanks

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Longclose Hank Dyeing Machines for carpet yarn, hand knitting yarns and hosiery yarns are available with capacities from 5/5000 lb. per batch. The Longclose Pressure System dyes cheeses, cones, Viscose Rayon Cakes, warps and hanks with batch capacities from 1/1000 lb. Plant suitable for all types of spun and continuous filament yarns supplied, including machines allowing use of temperatures exceeding 130° C. Standard beam dyeing units for one, three or four beams — with pre- and after-treatment plant. Specialised plant for Viscose Rayon Cake Dyeing.

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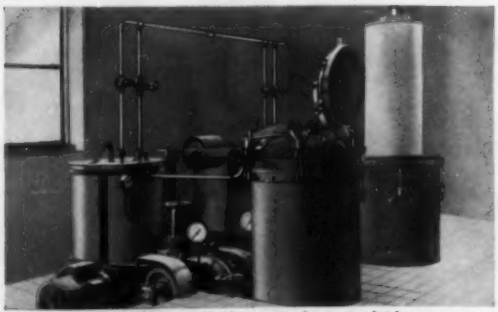

Beam Dyeing Plant available as single or multi-beam units

The Longclose 'Courtaulds Design' Rayon Cake Dyeing machine—300 lb. capacity units

FORTHCOMING MEETINGS OF THE SOCIETY — *continued from page* xii

Friday, 20th January 1956

MANCHESTER SECTION. *The Finishing of 'Terylene' Polyester Fibre Staple and Filament Fabrics.* G. D. Myers, Esq., B.Sc.Tech. Textile Institute, 10 Blackfriars Street, **Manchester 10.** 6.30 p.m.

WEST RIDING SECTION. Ladies' Evening. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Thursday, 26th January 1956

WEST RIDING SECTION. Details later. The Hotel Metropole, King Street, **Leeds.** 7.30 p.m.

Monday, 30th January 1956

BRADFORD JUNIOR BRANCH. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Coventry Ltd.). Technical College, **Bradford.** 7.15 p.m.

Thursday, 2nd February 1956

SCOTTISH SECTION. *Scouring and Milling.* B. F. J. Moxon, Esq. (Wool Industries Research Association). The Scottish Woollen Technical College, **Galashiels.** 7 p.m.

Friday, 3rd February 1956

LONDON SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Ltd., Coventry). Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

Wednesday, 8th February 1956

NORTHERN IRELAND SECTION. *General Principles in Vat Dyeing.* J. W. Reidy, Esq. (Messrs. L. B. Holliday & Co. Ltd.). (Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Thursday, 9th February 1956

WEST RIDING SECTION. *The Dyeing and Finishing of 'Terylene' and 'Terylene'/Wool Blended Fabrics.* H. R. Hadfield, Esq., M.Sc.Tech. and G. D. Myers, Esq., M.Sc.Tech. (Imperial Chemical Industries Limited, Dyestuffs Div., and Terylene Council). The Victoria Hotel, Bridge Street, Bradford. 7.30 p.m.

Tuesday, 14th February 1956

SCOTTISH SECTION. *The Dyeing and Finishing of 'Terylene' and 'Terylene' Blends.* J. G. Graham, Esq., and Dr. P. T. Standring (I.C.I. 'Terylene' Council). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Wednesday, 15th February 1956

BRADFORD JUNIOR BRANCH. *Piece Scouring.* B. F. J. Moxon, Esq. (Wool Industries Research Association). Technical College, **Bradford.** 7.15 p.m.

Friday, 17th February 1956

MANCHESTER SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq., B.Sc. Textile Institute, 10 Blackfriars Street, **Manchester 10.** 6.30 p.m.

NORTHERN IRELAND SECTION. Dinner Dance. Details later, at Woodbourne House Hotel.

Monday, 20th February 1956

HUDDERSFIELD SECTION. *The Finishing of 'Terylene' and 'Terylene' Wool Blended Fabrics.* N. M. Mims, Esq., B.A., B.Sc. (Joint Lecture with the Huddersfield Textile Society). Large Hall, Technical College, **Huddersfield.** 7.30 p.m.

Thursday, 23rd February 1956

MIDLANDS SECTION. *The Finishing of 'Terylene' and 'Terylene'/Wool Blends.* I. E. Haden, Esq., B.Sc., and B. I. Brooke, Esq., B.A.(Oxon.). Gas Theatre, **Nottingham.** 7 p.m.

NORTHERN IRELAND SECTION. *Film Evening.* Thompson's Restaurant, Donegall Place, **Belfast.** (Joint Meeting with the Textile Institute.) 7.30 p.m.

WEST RIDING SECTION. *Progress in the Cibalan Dye Range and their Application.* Clayton Dyestuffs Co. Ltd. Lecturer details later. The Victorial Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 2nd March 1956

LONDON SECTION. *Basic Mechanisms of Fading of Dyed Textiles.* H. B. Mann, Esq. (Courtaulds Ltd., Bocking). Royal Society Rooms, Burlington House, Piccadilly, **London, W.1.** 6 p.m.

BRADFORD JUNIOR BRANCH. Annual Dance. Connaught Rooms, **Bradford.**

Thursday, 8th March 1956

WEST RIDING SECTION. *A Commentary on the Use of Colour in Wool.* S. Morse-Brown, Esq. International Wool Secretariat. Ladies to be invited. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 9th March 1956

MIDLANDS SECTION. MIDLANDS SECTION DINNER. Bull's Head Hotel, **Loughborough.**

Tuesday, 13th March 1956

SCOTTISH SECTION. *The Soiling of Synthetic Fibres.* G. G. Taylor, Esq., B.Sc., A.Inst.P. (Clayton Dyestuffs Co. Ltd.). St. Enoch's Hotel, **Glasgow.** 7 p.m.

BRADFORD JUNIOR BRANCH. *Some Aspects of Continuous Vat Dyeing.* Dr. R. J. Rallings (British Cotton Industries Research Association). Technical College, **Bradford.** 7.15 p.m.

Wednesday, 14th March 1956

NORTHERN IRELAND SECTION. *Various Methods of Stripping Vat, Azoic, Direct and Sulphur Dyes.* J. E. Riordan, Esq. (College of Technology, Belfast.) *Effect of pH on the Activity of Bleaching Agents.* J. Boyd, Esq. (College of Technology, Belfast). Thompson's Restaurant, Donegall Place, **Belfast.** 7.30 p.m.

Tuesday, 20th March 1956

HUDDERSFIELD SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. (Courtaulds Ltd.). Co-operative Cafe, **Huddersfield.** 7.30 p.m.

Wednesday, 21st March 1956

MIDLANDS SECTION. *Fast Dyes on Cellulose Triacetate.* J. G. Graham, Esq., B.Sc. (Joint Meeting with British Association of Chemists). Midlands Hotel, **Derby.** 7 p.m.

Thursday, 22nd March 1956

MIDLANDS SECTION. *Dyeing Faults in the Carpet and Hosiery Industries.* G. H. Lister, Esq., B.Sc., Ph.D. (Joint Meeting with the Textile Institute). Carpet Trades Canteen, **Kidderminster.** 7 p.m.

WEST RIDING SECTION. ANNUAL GENERAL MEETING. The Victoria Hotel, Bridge Street, **Bradford.** 7.30 p.m.

Friday, 23rd March 1956

LONDON SECTION. *Dyeing of Narrow Fabrics — Cellulosic and New Fibres.* Dr. I. M. S. Walls (I.C.I. Ltd.). George Hotel, **Luton.** 7 p.m.

Saturday, 24th March 1956

NORTHERN IRELAND SECTION. Annual General Meeting and Dinner. Details later.

Tuesday, 10th April 1956

SCOTTISH SECTION. *Textile Invention and the Dry Cleaner.* A. J. Crockatt, Esq., M.Sc., F.R.I.C. (Eastmans Dyers and Cleaners Ltd.). St. Enoch's Hotel, **Glasgow.** 7 p.m.

Saturday, 21st April 1956

BRADFORD JUNIOR BRANCH. Annual General Meeting. Technical College, **Bradford.** 10.15 a.m.

Wednesday, 25th April 1956

HUDDERSFIELD SECTION. Visit to Messrs. Stevensons Dyers Ltd., **Ambergate,** Derbys.

MIDLANDS SECTION. *A New Approach to High Temperature Dyeing.* S. N. Bradshaw, Esq. Kings Head Hotel, **Loughborough.** Preceded by the Annual General Meeting of the Section. 6.30 p.m.

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Beetle Resins BT 309 and BT 321, used alone or in combination with Beetle Resin BT 320, stiffen nylon frills, flounces and pleats, keep them firm or stiff through the rigours of dry cleaning, of washday after washday after washday. The customer seeks this durability. See that she gets it, and that your garments or fabrics are suitably labelled so that she **knows** when she buys.

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Persons desirous of joining the Society as Ordinary Members or Junior Members may obtain Application Forms from the Secretary, or from the Honorary Secretary of any Section of the Society

NEW MEMBERS

Burns, G. A., c/o Messrs. Burns Dye Works Pty. Limited, 11/15 Foss Street, Forest Lodge, N. S. Wales, Australia

Coupe, R., Holly Dene, 31 Bury Old Road, Heywood, Lancs.

Cronin, J. P., 22 Northolme Avenue, Bulwell, Nottingham

Dominguez, G. S., Geigy Dyestuffs, Division of Geigy Chemical Corporation, 89 Barclay Street, New York 8, N.Y., U.S.A.

Dubuisson, A. A., Centre Scientifique et Technique de l'Industrie Textile Belge, 24 rue Montoyer, Bruxelles, Belgium

Fischer, A., Kiryat Bialik, Zur Shalom, 12 Rakafot Str., Haifa, India

Hodgson, C. S., c/o Messrs. Blundell Bros. (Luton) Limited, Chaul End Lane, Luton, Beds.

Humphreys, Dr. A. R., c/o The Geigy Company Limited, 14 Alfred Street, Belfast, Northern Ireland

Kadri, S., 9 Jinnah Co-operative Housing Society, near Central Jail, Karachi, Pakistan

McDonald, R., 36 Kilnside Road, Paisley, Renfrewshire

Sinclair, R. S., 41 Cruachan Street, Thomliebank, Glasgow

Speak, C., c/o Prospect Manufacturing Company Limited, Walter Street, Blackburn

Taylor, R. A., c/o Shell Chemicals Limited, 39 Corporation Street, Birmingham 2

Waddington, W., 3 Victoria Avenue, Shipley, Yorks.

Wallace, A., 17 Burnham Avenue, Burnage, Manchester 19

MEMBERS' CHANGES OF ADDRESS

Boothroyd, A. E., formerly of 43 Northgate, Baildon, to 55 Northgate, Baildon

Carlson, W. H., formerly of 208 Jackson Avenue, N. Augusta, S.C., U.S.A., to 523 Brookside Avenue, North Augusta, S.C., U.S.A.

Dickinson, K., formerly of 16 Hollycroft, Hinckley, to Redcroft, Boysdale Road, Burbage, Hinckley, Leics.

Everest, Dr. A. E., formerly of Hillocks, Harmer Hill, near Shrewsbury, to Church Bank, Kington, Herefordshire

Ferguson, T. D., formerly of Altavista, Va, U.S.A., to 7 Dacres Road, Greenfield, near Oldham, Lancs.

Kennedy, J. G., formerly of 22 Park Avenue, Sale, Manchester, to c/o Mr Luftwich, 2 Chesterford Gardens, London N.W.3

Henderson, D., formerly of 16 Springhill Gardens, Shawlands, Glasgow S.1, to 289 Kingsacre Road, Bankhead, Ruthergien, Glasgow

Holmebakk, G. A., formerly of 23 Merton Road, Great Horton, Bradford, to c/o Mr Baker, 120 Lewis Road, Droylsden, Manchester

Jones, W. H., formerly of 8 Green Lane, Belper, Derbys., to "Lyndhurst", 79 Newbridge Road, Ambergate, Derbys.

Leigh, J., formerly of 126 Hackett Place, Rutherford, N.J., U.S.A., to 230 Whitford Avenue, Nutley, New Jersey, U.S.A.

Macormac, A. R., formerly of Box 352, College Park, Maryland, U.S.A., to Assoc. Prof. of Home Economics, Box 1465, University, Alabama, U.S.A.

Moore, G., formerly of 20 Welwyn Avenue, Wrose, Shipley, to 44 Silverdale Road, West Bowling, Bradford

Morton, N. G., formerly of 4 Emecote Place, Halifax, Yorks., to 22 Ashbourne Grove, Halifax, Yorks.

Pobereznik, R. J. P., formerly of 166 Wood Road, Pontypridd, Glam., to 14 George Street, Old Trafford, Manchester 16

Roberts, E. T., formerly of The Waterdale Dyeing & Finishing Co. Ltd., Mere Clough, Prestwich, Manchester, to "Sandycove", 29 Dales Lane, Whitefield, Manchester

Robinson, J. I., formerly of L. B. Holliday & Co. Ltd., Suite 26, Bank of Toronto Buildings, 1410 Guy Street, Montreal, Canada, to c/o L. B. Holliday & Co. of Canada Ltd., Aniline Dyestuffs, 127 St. Peter Street, Montreal, Quebec, Canada

Waller, J., formerly of Officers' Mess, 10 B.O.D., Melf 15, to 4 Chapel Street, Birdwell, Barnsley, Yorks.

Winkler, A., formerly of 192 Chapeltown Road, Leeds 7, to North Lodge, Wakefield Road, Swillington, Woodlesford, near Leeds

Wood, P., formerly of 6 Poplar Grove, Gomersal, near Leeds, to Rydings Hall, Birstall, near Leeds

Yeoman, H., formerly of 282 Wilbraham Road, Manchester 16, to 8 High Grove Road, Cheadle, Cheshire

ADDRESSES WANTED

Alcada, J. C., formerly of 9 Mornington Villas, Flat No. 4, Bradford 8

Crook, B., formerly of 196 Wentworth Street, W., Magog, Quebec

Crowther, D., formerly of 551 Leeds Road, Thackley, Bradford

Green, A. N., formerly of 19 Salcombe Road, Basford, Nottingham

Kesprek, A. E., formerly of 15 Huntley Street, Hamilton Street, Ontario, Canada

Meier, P. W., formerly of Oberwilerstrasse 38, Basle, Switzerland

Morrison, A., formerly of America Woollen Co., P.O. Box 930, Lawrence, Mass., U.S.A.

Nixon, I. G., formerly of Adriaan Goekooplaan, 105 Flat Gebouw Catsheuvel, The Hague, Holland

Standring, Dr. P. T., formerly of I.C.I. Ltd., 1200 St. Alexander Street, Montreal, Canada

Stiassny, K., formerly of 70 Bialik Street, Ramat Gan, Israel

Swift, F. S., formerly of 3 St. Annes Street, Ennis, Co. Clare, Eire

a Viscosa, C. I. S., formerly of Dvozione Centrale degh Etabiliment (Dott. Calandra), Via Sicilia 162, Roma, Italy

Warchol, W., formerly of 14 Sparford Avenue, off Wollaton Road, Nottingham

SITUATIONS VACANT AND WANTED *etc*

The Publications Committee is prepared to receive Advertisements relating to SITUATIONS VACANT, SITUATIONS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Situations Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

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The engagement of persons answering these advertisements must be made through a Local Office of the Ministry of Labour or a Scheduled Employment Agency if the applicant is a man aged 18–64 inclusive or a woman aged 18–59 inclusive unless he or she, or the employment, is excepted from the provisions of the Notification of Vacancies Order 1952.

City of Bradford Conditioning House
SENIOR TEXTILE ANALYST

APPLICATIONS are invited for this Superannuable post from suitably qualified candidates. The duties involve the physical and chemical testing of textile materials from fibre form to finished products. A sound, extensive, practical experience is required with ability to control technical staff (male and female) and to undertake work of an investigational character.

Preference will be given to candidates holding a University degree or the Associateship of the Textile Institute.

Salary will be in accordance with A.P.T. Division Grades III–IV (£600–£825 per annum), the commencing salary to be fixed according to qualifications and experience.

Applications accompanied by names of two referees and endorsed "Senior Textile Analyst" should reach me by Monday, 31st October 1955.

W. H. LEATHEM,
Town Clerk.

Town Hall, Bradford 1.

ANALYST (B.Sc., A.R.I.C. or equivalent) required for varied, interesting, mainly textile work in chemical laboratory of official testing establishment in pleasant South Manchester district. Apply for personal attention of Director, Box V81.

ASSISTANT CHEMIST (male), aged 26–32 years, required for large firm of Dyers and Cleaners, Liverpool area. Academic qualification in Chemistry or Textiles essential. Applicant should have at least 2–3 years Works experience. Box V80

KEEN young qualified textile technician/chemist required to assist in Laboratory development and technical servicing of well-established resin pigment printing and dyeing and copolymer finishing products. Apply in writing, giving full details of qualifications and experience to Personnel Officer, Scott Bader & Co. Ltd., Wollaston, Wellingborough, Northants.

PLASTICS CHEMIST OR TECHNOLOGIST. Petrochemicals Limited require a graduate with experience in the plastics field for work on the processing and product evaluation of low pressure polyethylenes. Contributory Staff Pension Scheme. Non-contributory Sickness and Accident Benefit Scheme. Applications in writing should be addressed to the Personnel Manager, Petrochemicals Ltd., Partington Industrial Estate, Urmston, Manchester.

TEXTILE TECHNOLOGIST. Tootal Broadhurst Lee Co. Ltd. require a textile technologist for the position of Works chemist in their new factory in Tasmania. The person appointed would be responsible for textile testing and quality control and the investigation of colour application problems. Apply giving details of age, education, qualifications and experience to the Personnel Manager, 56 Oxford Street, Manchester.

WANTED Fully qualified and experienced DYER for all classes of PILE FABRICS. Good salary and prospects for right man. Apply Box V79.

SITUATIONS WANTED

MEMBER, aged 44, 25 years' experience preparing, dyeing, finishing rayon, cotton, and mixtures in piece goods. Terminating South American contract. Available interview Britain in December. Box W552

YOUNG MAN, 3 years' dyeing experience, exempt National Service. O.N.C. Inter-City & Guilds Pass. Desires position as apprentice for assistant dyer. Box W553

THE SOCIETY OF DYERS AND COLOURISTS

ANNUAL DINNER

will be held on

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This will be the Diamond Jubilee Year of the Manchester Section of the Society and the Perkin Centenary Year

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SEXTOL helps to dissolve Lime Soap and also assists detergents by reducing the surface tension of the water.

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Boiling Range (95%)	165°—180° C.
Specific Gravity (15.5° C.) . . .	0.925
Flash Point	145° F.
Evaporation Rate	807
Solubility of Sextol in water . . .	1.1%
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CHARACTERISTICS

Sextol is miscible with the usual detergents, soaps and Sulphated Fatty Alcohols and increases their detergent action. It is also a solvent for natural and synthetic resins, oils and dyes and improves the normal processes of scouring, printing and dyeing. It is non-explosive, non-toxic, non-corrosive and safe to handle.

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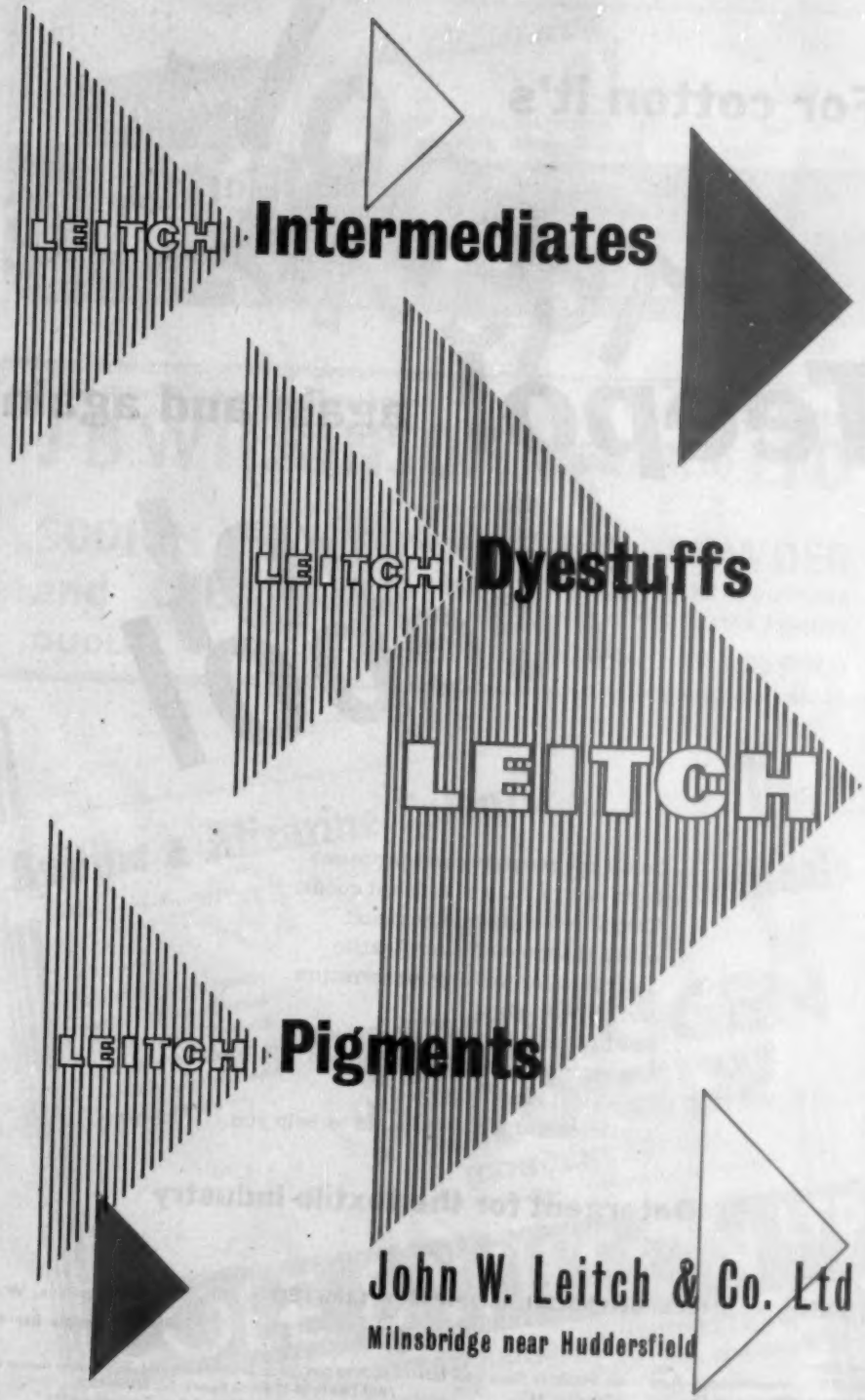
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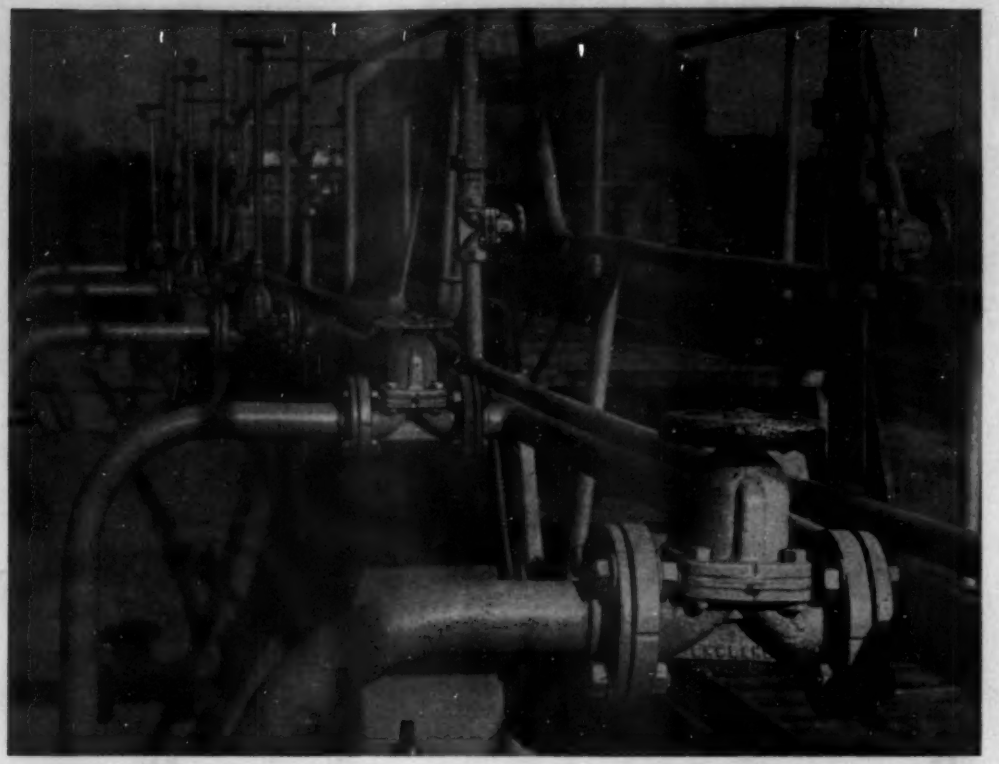

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INDEX TO ADVERTISERS

Page	
i	Albright & Wilson Ltd
xxiii	Bayer Leverkusen Germany
xxxii	B.I.P Chemicals Ltd
ii	British Drug Houses Ltd
xix	Brotherton & Co Ltd
xxxvi	Brown & Forth Ltd
xxii	Ciba Ltd
xxvii	Clayton Dyestuffs Co Ltd
xxxix	Cole & Wilson Ltd
ii	Colne Vale Dye & Chemical Co Ltd
xxi	Norman Evans & Rais Ltd
xxv	Farbwerke Hoechst A G
xxxiv	Chas. Forth & Son Ltd
xli	Gardinol Chemical Co Ltd
xviii	Geigy Co Ltd
xxxvi	Gemec Chemicals Co
Cover	Hardman & Holden Ltd
ix	L B Holliday & Co Ltd
xxxv	Howards of Ilford
xiv	Imperial Chemical Industries Ltd
xx	Imperial Chemical Industries Ltd
ix	Johnsons of Hendon Ltd
iii	Laporte Chemicals Ltd
xxxvii	John W Leitch & Co Ltd
xxx	Longclose Engineering Co Ltd
v	Mono Pumps Ltd
iv	Newell (Chemicals) Ltd
xlii	Sir James Farmer Norton & Co Ltd
xi	Samuel Pegg & Son Ltd
xxxvi	L J Pointing & Son Ltd
xxiv	James Robinson & Co Ltd
xiii	Sandoz Products Ltd
xv	Sandoz Products Ltd
xl	Saunders Valve Co Ltd
iv	T Saville Whittle Ltd
xxxviii	Shell Chemical Co Ltd
v	Shirley Developments Ltd
xvi	F Smith & Co (Whitworth) Ltd
xxxix	Standard Chemical Co Ltd
xli	Staveley Iron & Chemical Co Ltd
ii	Stockport United Chemical Co Ltd
xvii	Joseph Stubbs Ltd
xxix	Tennants Textile Colours Ltd
x	W P Thompson & Co
xxviii	Town End Chemical Works Ltd
viii	West Indies Chemical Works Ltd
vi	Whiffen & Sons Ltd
xxxix	J B Wilkinson (Chemicals) Ltd
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